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**ADVANCED STREAMING AGENT  
DEVELOPMENT  
Volume I: Silicon Compounds**



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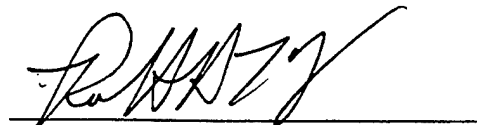
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## LIST OF ABBREVIATIONS

AAWG	Advanced Agent Working Group
ACGIH	American Conference of Governmental Industrial Hygienists
ARA	Applied Research Associates
BP	Boiling point
CAA	Chemical Action Agent
CAS	Chemical Abstracts Service (American Chemical Society)
CFC	Chlorofluorocarbon
CGET	Center for Global Environmental Technologies
FC	(Per)fluorocarbon
GWP	Global Warming Potential
HCFC	Hydrochlorofluorocarbons
HFC	Hydrofluorocarbons
HR	SAX Hazard Rating
LSDE	Laboratory-Scale Discharge Extinguishment
MP	Melting point
NMERI	New Mexico Engineering Research Institute
ODP	Ozone Depletion Potential
PAA	Physical Action Agent
PFC	Perfluorocarbon
PSHC	Polysilahydrocarbon
STEL	Short-Term Exposure Limit
TLV	Threshold Limit Value
TWA	Time Weighted Average
USAF	U.S. Air Force
VMS	Volatile methylsiloxane

## LIST OF UNITS AND SYMBOLS

cm	centimeter
cp	centipoise
cSt	centistoke
$C_t$	concentration at any time $t$
$C_o$	initial concentration
$e$	base of "natural" logarithmic system (2.71828...)
g	gram
hr	hour
<i>i</i>	<i>iso</i>
K	Kelvin
kg	kilogram
kJ	kilojoule
$k_2$	first-order reaction rate constant
L	liter
$LC_{Lo}$	lowest concentration causing death
$LC_{50}$	concentration required to cause death in 50 percent of an animal test population
$LD_{Lo}$	lowest dose causing death
$LD_{50}$	dose required to cause death in 50 percent of an animal test population
M	third-body molecule
m	meter
mg	milligram
min	minute
mL	milliliter
mol	mole
$N_F$	number of fluorine atoms in a molecule
$N_H$	number of hydrogen atoms in a molecule
$n$	normal
pm	picometer = $10^{-12}$ meters
ppm	parts per million

## LIST OF UNITS AND SYMBOLS (concluded)

s	second
<i>s</i>	secondary ( <i>sec</i> )
<i>t</i>	tertiary ( <i>tert</i> )
W	watt
X	halogen atom
•R	free radical (R is any alkyl group)
:R	carbene (R is any carbenyl group)
μg	microgram
$\Delta H_{\text{comb}}$	heat of combustion

## PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico 87131, for the Infrastructure Technology Section of Wright Laboratory (WL/FIVCF), Tyndall Air Force Base, and Applied Research Associates (ARA), Inc., Tyndall Air Force Base, under SETA Task 3.12, Air Force Contract S-5000.31, NMERI Number 8-32540. This document is Volume I of the final report and provides an assessment of silicon compounds as potential substitutes for replacement of Halon 1211 in streaming applications.

The Start Date for the overall Advanced Streaming Agent Program was 9 August 1995, and the End Date is April 30 1996. The WL/FIVCF Project Officer is Capt. Robert A. Tetla, the ARA Project Officer is Michael A. Rochefort, and the NMERI Principal Investigator is Robert E. Tapscott.

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## EXECUTIVE SUMMARY

### A OBJECTIVE

The objective of the overall effort is to develop new chemical compounds that are highly efficient fire suppressants, are environmentally and toxicologically benign, have the same performance characteristics as Halon 1211, and are compatible with existing fire extinguishing equipment and aircraft materials. The effort includes (1) synthesis of the new compounds; (2) laboratory analysis of fire suppression characteristics; (3) analysis of environmental and toxicity parameters; and (4) analysis of stability, compatibility, and manufacturability factors. The outcome of the effort is the identification of the most promising replacement candidates for follow-on medium- and large-scale testing.

This document is Volume I of the final report and provides an assessment of silicon compounds as potential substitutes for replacement of Halon 1211 in streaming applications. The five volumes of the final report are listed below:

Gobeli, G. W., Tapscott, R. E., and Kaizerman, J. A., *Advanced Streaming Agent Development, Volume I: Silicon Compounds*, WL-TR-96-XX, Vol. 1 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996. NMERI 96/1/32540

Patterson, R. A., Gobeli, G. W., Brabson, G. D., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume II: Metal Compounds*, WL-TR-96-XX, Vol. 2 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/3/32540

Kaizerman, J. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume III: Phosphorus Compounds*, WL-TR-96-XX, Vol. 3 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/5/32540

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## B. BACKGROUND

Under the Montreal Protocol, an international treaty enacted in 1987 and amended in 1990, 1992, and 1995, the production of the fire and explosion protection agents Halon 1211 (bromochlorodifluoromethane, BCFC-12B1,  $\text{CBrClF}_2$ ) and Halon 1301 (bromotrifluoromethane, BFC-13B1,  $\text{CBrF}_3$ ) was phased out in the United States at the end of 1993.\* To date, no environmentally acceptable halon substitute, equivalent to the existing halons in toxicity, effectiveness, and dimensionality, has been identified.

Halocarbons as replacements for halons have been well studied, and it is unlikely that new, exceptionally effective, halon replacements will be identified among the standard, saturated, non-iodinated halocarbons. The hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC or FC), and hydrofluorocarbons (HFC) are all less effective than the present halons in most scenarios and usually exhibit higher toxic gas emissions during fire suppression. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs. The single partial success among halocarbon replacements are the iodides, in particular, trifluoromethyl iodide ( $\text{CF}_3\text{I}$ ), which is as effective as the existing halons. However, the cardiosensitization of the fluoroalkyl iodides that have been investigated restricts their use to only certain applications. There is, therefore, an increasing incentive to look at compounds other than the usual, saturated halocarbons. These compounds are the non-halocarbon candidates, known as "advanced agents." The most promising of these are the phosphorus compounds (particularly, the phosphorus nitrides, which include

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\*See Volume IV of this series of reports for an overview of halocarbon numbers (e.g., BCFC-12B1 and BFC-13B1) and general information on halocarbon nomenclature.

phosphazenes, phosphonitriles, and phosphazanes), metal compounds, and silicon compounds. In addition, the special class of tropodegradable halocarbons includes promising candidates.

## C. SCOPE

An investigation of advanced fire suppression agents is being conducted to find a replacement for Halon 1211 used in U.S. Air Force (USAF) flightline and portable fire extinguishers. Four separate tasks are included in the present overall effort:

Task 1: Technical Review. A technical review of syntheses, characterization, properties, toxicity, and fire extinguishment data (if any) for phosphorus nitrides, metal compounds, and silicon compounds that may have utility as fire and explosion protection agents is to be conducted.

Task 2: Synthesis of New Compounds. Samples of the most promising of these materials based on expected toxicity, availability/manufacturability, and environmental characteristics are to be prepared or obtained.

Task 3: Laboratory Evaluations. Laboratory-scale evaluations of fire extinguishment by these materials are to be performed. Preliminary analyses of global environmental impact, toxicity evaluations, and manufacturing/synthesis assessment of the candidates identified for follow-on testing are to be conducted.

Task 4: Final Report. The information obtained is to be used to prepare a final report detailing the work performed, the results obtained, and conclusions. The report will make recommendations for continuation of large-scale testing with the most promising agents.

## D. METHODOLOGY

Relevant information on silicon compounds as potential substitutes for Halon 1211 was collected and assessed using a thorough review of the chemical literature. The review included the synthesis and physical properties of silicon and siloxane compounds with an emphasis on compounds containing alkyl, haloalkyl, alkoxy, and haloalkoxy substituents. Estimation methods



were applied to assess global environmental characteristics, specifically Global Warming Potentials (GWP) and Ozone Depletion Potentials (ODP).

#### E. APPROACH

Silicon compounds have lower atmospheric lifetimes than do the closely related carbon compounds. Thus, all other things being equal, GWPs and ODPs are expected to be lower. In fact, it is not unlikely that one can incorporate bromine in silanes and siloxanes without having unacceptably large ODPs. To avoid toxicity and stability problems, however, it is essential that halogen atoms (fluorine, chlorine, bromine, and iodine) not be attached directly to the silicon atom. Such molecules are highly susceptible to hydrolysis in moist air with the formation of hydrogen halides. Compounds containing haloalkyl groups such as  $-\text{CF}_2\text{Br}$ , where halogen atoms are attached only to carbon and do not hydrolyze rapidly, can be considered. It is important to keep the number of hydrogen atoms as low as possible to decrease flammability. With these criteria in mind, a review of the properties and syntheses of silicon compounds has been completed with an emphasis on those that either contain bromine or could be used as skeletons for attachment of suitable bromine-containing groups. This review also includes a comparison of the atomic and bonding properties of silicon with related elements. A thorough analysis of the parameters affecting the global environmental characteristics was also performed.

#### F. RESULTS

Analyses and estimation methods indicate that silicon compounds containing bromocarbon substituents should have atmospheric lifetimes on the order of days and ODPs of less than 0.02. Since these materials are expected to have only one primary commercial application (fire suppression), it is likely that their use would not be significantly restricted due to their global environmental effects. Two groups of silicon compounds are found to be of particular interest—silanes (which are analogous to the carbon-containing alkanes) and siloxanes (which contain one or more Si-O-Si groups). Alkoxy derivatives are particularly promising because of their enhanced stability and the potential for increased degradation in the troposphere owing to enhanced abstraction of hydrogen atoms adjacent to the oxygen atom by tropospheric hydroxyl free radicals.

## G. CONCLUSIONS

Silicon-based materials containing bromine are expected to provide good fire extinguishment, comparable to the halons. The atmospheric lifetimes, ODPs, and GWPs should be sufficiently low that the compounds are environmentally acceptable. The major uncertainties are the manufacturability and the toxicity. It is known that the toxicities of many of the parent compounds are very low; however, bromination may increase the toxicity. In general, these compounds are more difficult to manufacture than the tropodegradable halocarbons and the metal compounds, which are discussed in other volumes of this report. In general, fluorination is expected to improve volatility, fire suppression performance, and, in some cases, toxicity. However, compounds containing fluorine on a carbon atom adjacent to silicon are inherently unstable, and this may be a major problem associated with synthesis and use.

The compounds recommended for evaluation include both silanes and siloxanes; however, the siloxanes may be more acceptable from the standpoint of both toxicology and stability.

Compounds containing silicon-nitrogen bonds also appear attractive as halon alternatives. Such materials, which are very briefly reviewed in this report, often have good stabilities and may provide excellent frameworks for attachment of bromine. Their chemistry, in many cases, is analogous to the siloxanes.

## H. RECOMMENDATIONS

Work should continue on silicon compounds with an emphasis on those compounds specifically recommended in this report for further testing and evaluation. Synthetic work is particularly important since it is likely that each separate compound will require synthetic steps unique to that material. Compounds containing silicon-hydrogen and silicon-halogen bonds should not be considered as candidates, though they may be useful as precursors. Consideration should also be given to the potential of silazenes, compounds containing silicon-nitrogen bonds.

In addition, photolytic cross sections should be determined for the materials recommended in this study or for closely related compounds. Silicon and bromine combined in the same molecule may have a synergistic effect on photolytic cross sections.

Toxicity studies, particularly to determine  $LC_{50}$  or  $LC_{LO}$  values, should be carried out on selected compounds recommended for testing.

## SECTION I

### INTRODUCTION

#### A. OBJECTIVE

The objective of the overall effort is to develop new chemical compounds that are highly efficient fire suppressants, are environmentally and toxicologically benign, have the same performance characteristics as Halon 1211, and are compatible with existing fire extinguishing equipment and aircraft materials. The effort includes (1) synthesis of the new compounds; (2) laboratory analysis of fire suppression characteristics; (3) analysis of environmental and toxicity parameters; and (4) analysis of stability, compatibility, and manufacturability factors. The outcome of the effort is the identification of the most promising replacement candidates for follow-on medium- and large-scale testing.

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Halocarbons as replacements for halons have been well studied, and it is unlikely that new, highly effective, halon replacements will be identified among the typical non-iodinated haloalkanes. The hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC or FC), and hydrofluorocarbons (HFC) are all less effective than the present halons in most scenarios. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs (for an overview, see Reference 1). The single partial success among halocarbon replacements are the iodides, in particular, trifluoromethyl iodide ( $\text{CF}_3\text{I}$ ), which is as effective as the existing halons. However, the toxicity of the iodides restricts their use to only certain applications. There is, therefore, an increasing incentive to look at compounds other than the typical haloalkanes. These compounds are the non-halocarbon candidates, known as "advanced agents" and a special class of halocarbons, the "tropodegradable" halocarbons.

Recent work has identified several potential non-halocarbon (References 2 and 3) and low-atmospheric-lifetime halocarbon (Reference 4) substitutes for halon fire extinguishants. In particular, work by the Advanced Agent Working Group (AAWG), which includes U.S. Air Force (USAF) and U.S. Army participation, has shown that the most promising of the non-halocarbon compounds are phosphorus compounds (particularly, phosphorus nitrides, which include the phosphazenes, phosphonitriles, and phosphazanes), metal compounds, and silicon

compounds (Reference 5). The AAWG work (which emphasizes chemical options for total-flood Halon-1301 applications) and work by the USAF also shows that tropodegradable halocarbons, which contain features that induce short atmospheric lifetimes, exhibit high promise.

### C. SCOPE

An investigation of advanced fire suppression agents is being conducted to find a replacement for Halon 1211 used in USAF flightline and portable fire extinguishers. Four separate tasks are included in the present overall effort:

Task 1: Technical Review. A technical review of syntheses, characterization, properties, toxicity, and fire extinguishment data (if any) for phosphorus nitrides, metal compounds, and silicon compounds that may have utility as fire and explosion protection agents is to be conducted.

Task 2: Synthesis of New Compounds. Samples of the most promising of these materials based on expected toxicity, availability/manufacturability, and environmental characteristics are to be prepared or obtained.

Task 3: Laboratory Evaluations. Laboratory-scale evaluations of fire extinguishment by these materials are to be performed. Preliminary analyses of global environmental impact, toxicity evaluations, and manufacturing/synthesis assessment of the candidates identified for follow-on testing are to be conducted.

Task 4: Final Report. The information obtained is to be used to prepare a final report detailing the work performed, the results obtained, and conclusions. The report will make recommendations for continuation of large-scale testing with the most promising agents.

This volume of the final report covers silicon compounds.

## SECTION II

### RATIONALE

Many organosilicon compounds are relatively stable, inert, and have a low toxicity. Of particular importance is that silicon compounds have lower atmospheric lifetimes than do the closely related carbon compounds. Thus, all other things being equal, Global Warming Potentials (GWP) and Ozone Depletion Potentials (ODP) are lower. In fact, it is likely that one can incorporate bromine in silanes and siloxanes without having unacceptably large ODPs, and this approach is evaluated in this study. Silicon compounds that do not contain bromine or other group providing chemical fire suppression (see below) do not appear to have a significant inherent fire suppression activity other than that provided by heat absorption and other physical processes.

In general, chemical fire suppressants can be divided into two types. Physical Action Agents (PAA) are those that operate primarily by heat absorption (and, to a lesser extent, separation of fuel from oxidant and dilution of air and vaporized fuel). Chemical Action Agents (CAA), such as the halons, are those that operate primarily by chemical means, i.e., removal of flame free radicals. The chemical effect contribution to extinguishment by PAAs is only 10 to 25 percent of the physical contribution (Reference 6). In general, CAAs are much more effective extinguishants than are PAAs, examples of which are the HCFCs, HFCs, and PFCs. Halons 1211 and 1301 are primarily CAAs. Work at the Naval Research Laboratory (NRL) indicates that Halon 1301 extinguishment of *n*-heptane in air is approximately 20 percent physical and 80 percent chemical (Reference 7). The analysis also indicates that about 25 percent of the extinguishment is due to the CF<sub>3</sub> group and about 55 percent is due to the bromine. Though CAAs are more effective, they often have higher ODPs because they frequently contain bromine. Nevertheless, the objective of AAWG and of recent USAF efforts is to find environmentally acceptable CAAs, since it appears that only such candidates offer the promise of agents equivalent to the present halons in effectiveness, widespread applicability, and dimensionality.

With the exclusion of iodine, which provides a low atmospheric lifetime as a result of photolysis without the need for the silicon framework (Reference 8), bromine is the halogen providing an optimal fire extinguishment capability and is the basis for most of the proven CAAs (Reference 9). The primary mechanism for chemical inhibition of hydrocarbon flames for halons and similar CAAs is believed to be removal of highly reactive free radicals that maintain combustion; e.g., hydrogen atoms ( $\bullet\text{H}$ ), hydroxyl free radicals ( $\bullet\text{OH}$ ), and oxygen atoms ( $\bullet\text{O}$ ). Based on the relative abundance of these three species and their importance in driving combustion, it is generally believed that hydrogen-atom removal is the most effective inhibition pathway, followed by removal of hydroxyl free radicals, and finally removal of oxygen atoms. The relative importance of these three processes is still debated, however, and may depend on the fuel and flame characteristics. Removal of hydrogen atoms has a particularly large effect due to the role that hydrogen plays in the primary chain-branching reaction (Reaction 1) that sustains combustion of hydrocarbon fuels (Reference 10).



Westbrook has proposed that a primary process for inhibition of hydrocarbon flames by halogen-containing species is a catalytic combination of hydrogen atoms by hydrogen halides (Reference 11). This is shown below, where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}^*$



Here, "M" represents any third-body molecule that carries off energy from the recombination of halogen atoms ( $\bullet\text{X}$ ), giving an activated molecule ( $\text{M}^*$ ) with increased vibrational, rotational, and/or translational energy.

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\*Actually, it is doubtful that F or Cl enters into a catalytic cycle. This is discussed further on.



Since bond strength decreases in the order H-F, H-Cl, H-Br, and H-I, iodine and bromine are the most effective and fluorine and chlorine are the least effective in the catalytic cycle represented by Reactions 2 through 4. In fact, once H-F, or possibly H-Cl, is formed in Reaction 2, the halogen is no longer available for participation in Reaction 3. This can be seen from a comparison of the bond energies for the various species involved in Reaction 3 (Reference 12). These energies show that Reaction 3 is distinctly endothermic for X = F and is only slightly exothermic for X = Cl (Table 1).

TABLE 1. BOND ENERGIES FOR HYDROGEN HALIDES AND DIATOMIC HYDROGEN.

Diatomic molecule	Bond energy, kJ/mol
H-H	435.99
H-F	570.3
H-Cl	431.62
H-Br	366.35
H-I	298.407

The net result of the catalytic cycle given by Reactions 2 through 4 is the combination of two hydrogen atoms to form "relatively inactive" diatomic hydrogen.\*



In the case of inhibition by halocarbons, the initial reaction is believed to be a free-radical abstraction of a halogen atom by atomic hydrogen to form HX. The overall process is illustrated for Halon 1301, CF<sub>3</sub>Br, in Reactions 6 through 9. A similar mechanism is expected to hold for extinguishment by bromine-containing silicon compounds.




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\*Relatively inactive in comparison to the highly reactive hydrogen free radicals (hydrogen atoms).



Thus, unless other components are present that provide chemical fire suppression (e.g., phosphorus nitrides, metals), bromine is needed for a chemically active agent. The following structural considerations are important in obtaining silicon compounds acceptable as fire extinguishants:

1. To avoid toxicity and stability problems, halogen atoms (fluorine, chlorine, bromine, and iodine) should not be attached directly to the silicon atom (such compounds may, however, be used as baseline materials for development of extinguishment concepts and as synthetic precursors). Molecules containing direct silicon-halogen bonds are highly susceptible to hydrolysis with the formation of hydrogen halides. In fact, it has been stated that "This effect is so pronounced that the presence of a single silicon-halogen bond in a molecule is sufficient to make its vapors corrosive and dangerous to breathe" (Reference 13).

2. To provide a chemically active fire suppressant, bromine is needed. This may be incorporated in groups such as  $-\text{CF}_2\text{Br}$ , where halogen atoms are attached only to carbon and are kinetically resistant to hydrolysis.

3. Volatility, usually a desirable property, increases with the hydrogen content. Increased hydrogen content, however, also leads to increased flammability and decreased effectiveness as a fire extinguishing agent. Thus, it is important to keep the number of hydrogen atoms as low as possible.

4. In general, fluorine substitution leads to a lower toxicity than does chlorine substitution. In addition, fluorine substitution will, in general, yield compounds with a higher volatility (desirable here) than will chlorine substitution.

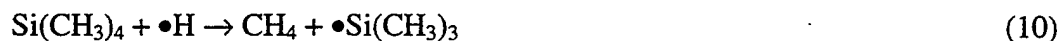
With these guidelines in mind, a review of the properties and syntheses of silicon compounds was undertaken with an emphasis on those that either contain bromine or could be used as skeletons for attachment of suitable bromine-containing groups. Two families of compounds—silanes (analogous to the carbon-containing alkanes) and siloxanes (which contain one or more Si-O-Si groups)—are emphasized. The substances of greatest interest are those in which at least one alkyl or alkoxy group contains a bromine atom. Thus, molecules containing a bromine atom attached to alkyl and alkoxide substituents (probably fluorinated), along with additional fully, partially, or non-fluorinated groups as needed to satisfy the bonding requirements, are targeted. It may be possible to also allow compounds containing hydrogen atoms directly bonded to silicon; however, such compounds are generally less promising than those not containing this structural feature.

In addition to the major families, some information is presented on silicon/nitrogen compounds, which have some interesting and, possibly, promising characteristics.

### SECTION III

#### FIRE SUPPRESSION BY SILICON COMPOUNDS

Silicon compounds, particularly silicon tetrachloride,  $\text{SiCl}_4$ , have been included in a number of laboratory-scale extinguishment determinations. The peak in the flammability curve for silicon tetrachloride is 9.9 percent by volume for a premixed *n*-heptane flame (Reference 14). This value is a little lower than that of 11.5 percent for carbon tetrachloride,  $\text{CCl}_4$ , found in the same study; however, it indicates no special fire suppression ability for silicon. The Group IV halides  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ , and  $\text{SnCl}_4$  all decrease the burning velocities of stoichiometric *n*-hexane/air mixtures with the effectiveness increasing with molecular weight, as shown in Table 2 (Reference 15). Due to environmental and toxicological factors, however, silicon and carbon compounds are the only compounds of the Group IV elements that can be seriously considered as candidate fire suppression agents. The addition of a single hydrogen atom to  $\text{SiCl}_4$  to give  $\text{SiHCl}_3$  causes a large decrease in effectiveness at decreasing burning velocity. This may indicate that the presence of a Si-H bond is an undesirable feature in candidate replacements. That most of the compounds in Table 2 contain chlorine probably explains their burning velocity inhibition; however, this does not hold for tetramethyl silane,  $\text{Si}(\text{CH}_3)_4$ , which contains no chlorine. Here, however, it is likely that the methyl groups act as hydrogen scavengers such as in Reaction 10. Moreover, trimethylsilane is a fuel, and it is well known that addition of a fuel can act as a flame inhibitor under some very carefully defined conditions. For example, HFC-152a is flammable, but is one of the most effective HFCs for explosion inertion (Reference 16).



Some silicon compounds have been employed as fire retardant coatings on synthetic fibers employed in the fabrication of clothing, furniture coverings, rugs, etc.; however, this may be due to formation of an air barrier coating on the fiber rather than to a fire suppression mechanism inherent in silicon. Although polysiloxanes have been used in fire protection agent mixtures with phosphates and other materials, the amounts used are sufficiently small that the

TABLE 2. EFFECTIVENESS IN DECREASING BURNING VELOCITY  
OF *n*-HEXANE/AIR MIXTURE.

Compound	Amount required for 30% reduction in flame velocity	
	Volume %	Weight %
CCl <sub>4</sub>	1.38	6.65
SiCl <sub>4</sub>	0.56	3.07
GeCl <sub>4</sub>	0.50	3.44
SnCl <sub>4</sub>	0.19	1.61
SiHCl <sub>3</sub>	2.9	11.8
Si(CH <sub>3</sub> ) <sub>4</sub>	1.5	4.25

extinguishment capability may be due to the phosphate (References 17 and 18). A silicone resin has been announced as improving the flame retardance of polyolefins (References 19 and 20).

Two commercially available silicone fluids have been tested as potential aircraft hydraulic fluids (Reference 21), but were found to have overall fire performance properties that were relatively poor in comparison to other materials. The heats of combustion determined for the two fluids, of unspecified composition (probably methyl siloxanes), were  $\Delta H_{\text{comb}} = 22.65$  and  $22.70$  kJ/g. These values can be compared with values of approximately 44 to 49 kJ/g found for synthetic hydrocarbon fluids and 5 to 7 kJ/g determined for fluorocarbon fluids (probably perfluorocarbons) in the same study. The autoignition temperature determined for one of the silicone fluids was  $409^\circ\text{C}$ , which was slightly higher (better) than those of the hydraulic fluids in service at the time the report was written, but considerably lower than those of the fluorocarbons ( $1165$  to  $1190^\circ\text{C}$ ).

In summary, it does not appear that silicon compounds offer any significant inherent activity as CAAs due to the presence of silicon. In general, fire suppressant activity can be attributed to heat absorption and/or to substituents such as halogen atoms present in the silicon compound. This is, however, to be expected. The primary reason for examining silicon

compounds is that their atmospheric lifetimes are lower than those of the corresponding carbon analogs. Thus, by incorporating a constituent, namely bromine, that provides chemical fire extinguishment, one may be able to produce highly effective but environmentally acceptable fire extinguishants, even in the presence of bromine. This is discussed further in Section V.

## SECTION IV

### ATOMIC AND BONDING PROPERTIES

#### A. ATOMIC PROPERTIES

Silicon is the second member of the Group IV elements, which are comprised of carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb). The electronic configurations and nonpolar covalent radii of the Group IV elements are given in Table 3 (References 22 and 23). The covalent radius (the average radius of an atom in a covalent bond) of silicon lies closer to the radii of germanium and tin than to the radius of carbon. Electronegativity, another determining factor for the general chemistry of an element, describes the power of an atom in a molecule to attract electrons.\* Among the Group IV atoms, carbon is clearly the most electronegative. Silicon is sometimes said to be more electronegative, by a very small amount, than germanium or tin; however, more often silicon is accepted as being equal in electronegativity to these elements. Thus, from these relatively simplistic considerations, one might tend to group silicon more closely with germanium and tin than with carbon, and in general such a grouping tends to be accurate (Reference 24).

#### B. ELEMENTAL SILICON AND CARBON

Before considering compounds of silicon and carbon, it is useful to give a short account of the characteristic differences between the elemental properties. Elemental carbon is found as either diamond or graphite. Diamond is a nonconductor, or a semiconductor with an exceedingly large bandgap. Graphite is a conventional semiconductor. Elemental silicon, which is not freely

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\*Electronegativity is essentially a qualitative concept. Various methods have been proposed to quantify electronegativity based on measured or calculated properties, and, while some agreement is usually attained in the trends, the numerical values are often quite different. The Pauling electronegativities given here appear to be as useful as any and are the ones most often cited in simplified chemical assessments.

TABLE 3. ATOMIC PROPERTIES OF GROUP IV ELEMENTS.

Element	Electronic configuration	Nonpolar covalent, radius, pm	Pauling electronegativity
C	$1s^2 2s^2 2p^2$	77	2.60
Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	111	1.90
Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	122	1.90
Sn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$	140	1.90
Pb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$	147	1.8

available in nature and is produced by reduction of  $\text{SiO}_2$ , crystallizes in the diamond lattice and is a semiconductor.

### C. BONDING

It is also useful to compare the energies of carbon and silicon bonds with the same atoms. Some data are presented in Table 4 (References 27 and 25). Note that the Si-Si bond and Si-H bonds are weaker than the C-C and C-H bonds. On the other hand, bonds between silicon and halogen atoms and between silicon and oxygen are stronger than the corresponding carbon bonds. These data suggest that the Si-H bond is more reactive toward halogens and oxygen than is the C-H bond (i.e., Si-H is a stronger reducing agent than is C-H), and this is found to be the case.

Figure 1 provides a visual illustration of the various carbon and silicon bond energies and gives a thermodynamic demonstration that explains many of the differences between the analogs of carbon and silicon compounds of the types considered in this report.

In general, bond strengths tend to decrease with increasing atom size, as is seen in comparisons of both the C-H and Si-H bond strengths and the C-C, C-Si, and Si-Si bond strengths. The "anomalous" increase in bond strength going from carbon to silicon for bonds



involving oxygen and halogens is usually explained as follows. Bonded oxygen and halogen atoms have lone pairs of electrons (unlike bonded hydrogen, carbon, and silicon atoms), and it is generally proposed that the large bond strength for Si-O and Si-X (X = halogen) bonds is due to “back donation” of these lone pairs (which have primarily p atomic orbital character) into empty d orbitals on the silicon atom. This gives some double bond character to bonds between silicon and oxygen or halogen atoms. This additional bonding is often referred to as “ $p\pi \rightarrow d\pi$  bonding” (Figure 2).

TABLE 4. BOND ENERGIES.

Bond	Energy, kJ/mol	Bond	Energy, kJ/mol
Si-H	318	C-H	414
Si-Si	214	C-C	347
Si-C	301 (tetramethylsilane)		
Si-C	251 (tetraethylsilane)		
Si-C	327 (silicones)		
Si-F	565	C-F	486
Si-Cl	381	C-Cl	327
Si-Br	310	C-Br	285
Si-O (silica)	452	C-O	360
Si-O (silicones)	507		
<sup>1</sup> Si-CH <sub>3</sub>	352	<sup>2</sup> C-CH <sub>3</sub>	301

<sup>1</sup>Si(CH<sub>3</sub>)<sub>4</sub>.  
<sup>2</sup>C(CH<sub>3</sub>)<sub>4</sub>.

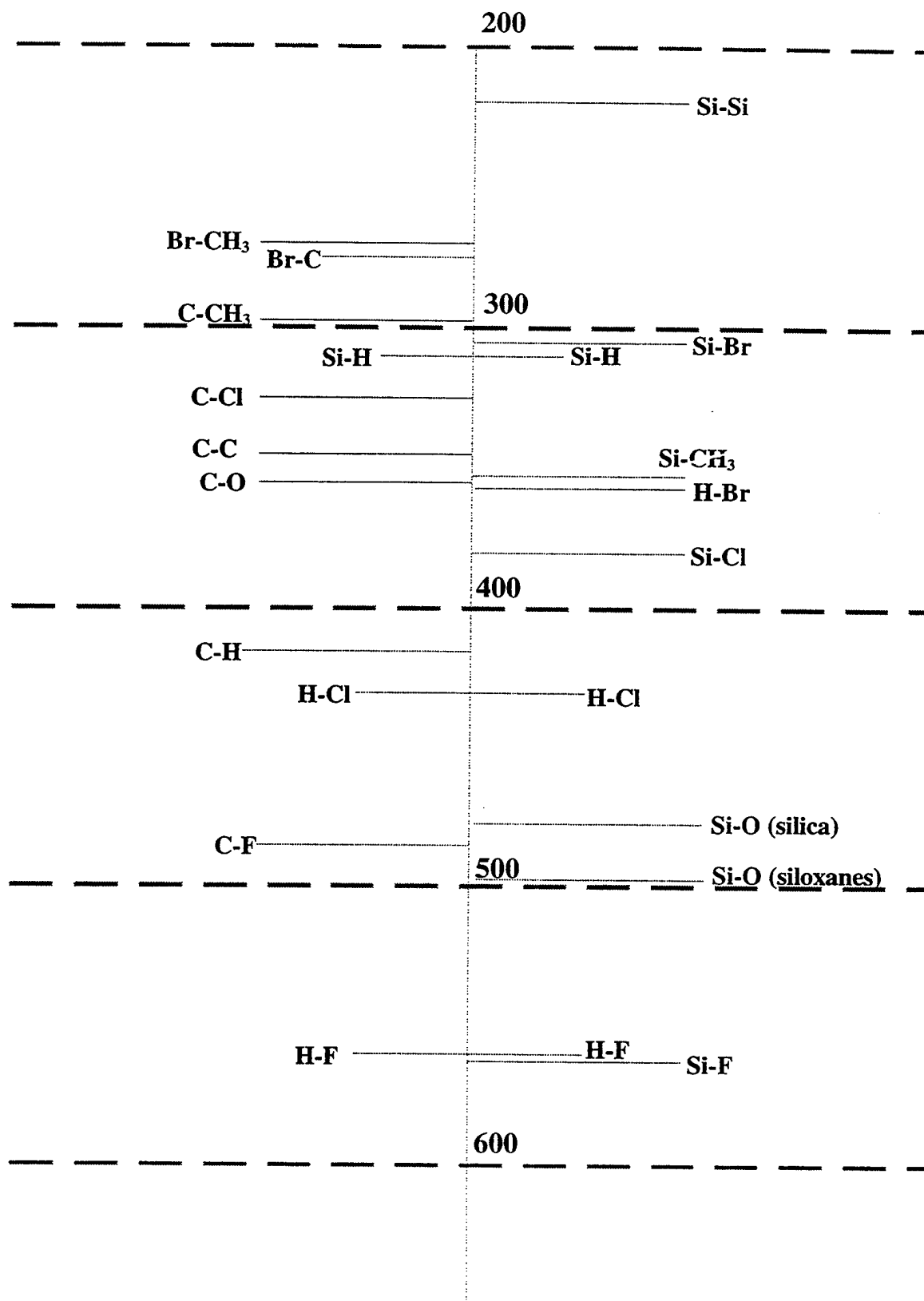


Figure 1. Carbon and Silicon Compound Bond Energies, kJ.

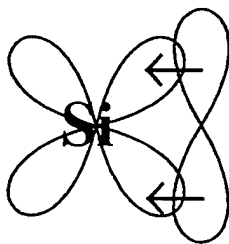


Figure 2.  $p\pi \rightarrow d\pi$  Bonding in Si-X (X = Halogen) and Si-O Bonds.

The large strength of the Si-O bond causes silicic acid\* or inorganic silicates to often be generated from reactions involving silicon compounds in the presence of air and water. Inorganic silicates are distinctly separate from the organic compounds considered in this report and have properties and uses that arise from the great strength of the Si-O bond (References 26 and 27). On the other hand, in living (carbon-based) systems, C-O, C-C, and C-H bond energies are close enough to allow enzymatically-controlled reaction pathways. The differences in the bond energies of Si-H, Si-Si, and Si-O do not permit analogous processes in silicon chemistry.

A further appreciation of the difference between carbon and silicon compounds can be obtained from consideration of the respective elemental electronegativities: Si, 1.9; C, 2.6; H, 2.2 (Pauling electronegativities [Reference 22]). Because the electronegativity of the hydrogen atom is greater than that of the silicon atom, the hydrogen atom in the Si-H bond maintains a hydridic character (i.e., there is a partial negative charge on hydrogen), while the hydrogen atom in the C-H bond has a positive partial charge. Similarly, the silicon atom in the Si-C bond is more positive than the carbon atom. Thus, in alkaline solution, substances containing Si-H bonds produce  $H_2$  with formation of Si-OH (Reaction 11), while under these conditions, the C-H bond is unaffected. Due to the electronegativity differences between silicon and carbon, silicon compounds, e.g., silicon halides, are often more polar than the corresponding carbon analogs.




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\*See Appendix A for definitions of the various chemical and other terms used in this report.

The differing electronic configurations of silicon and carbon must also be taken into consideration. Silicon d orbitals have energies that make possible the formation of pentavalent or hexavalent states. The availability of valence states in addition to the usual tetravalent state (sometimes referred to as "valence shell expansion") enhances the reactivity of silicon compounds. Thus, hydrolysis of silicon halides (e.g., Reaction 12, where X represents a halogen atom and R is any substituent) is much more rapid than that of carbon, which has a maximum valence of four, even though both reactions are thermodynamically favorable. The hydrolytic cleavage of the Si-halogen bond may proceed through a pentavalent transition state, which greatly lowers the activation energy and makes the reaction kinetically favorable (Figure 3).

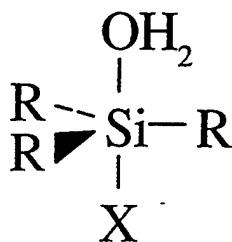


Figure 3. Pentavalent Transition State Proposed for Hydrolysis of a Silicon Halide.

#### D. COMPOUNDS OF SILICON

Fewer functional groups are found for silicon compounds than for carbon compounds. Functional groups in silicon compounds are confined primarily to Si-X, Si-H, Si-OH, Si-OR, Si-N, and Si-P. The Si-OH group, however, tends to eliminate H<sub>2</sub>O, forming Si-O-Si bonds. Silicon does not form stable  $p\pi \leftrightarrow p\pi$  (Figure 4) bonds (e.g., O=C=O exists, but O=Si=O does not). As noted earlier, however, silicon can form partial double bonds with some other elements through  $p\pi \rightarrow d\pi$  bonding.

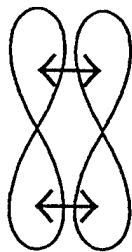


Figure 4.  $p\pi \leftrightarrow p\pi$  Bonding.

The chemistry of carbon is determined to a considerable degree not only by the many functional groups possible for its compounds, but also by its ability to form molecules with stable single C-C bonds, multiple C=C and C≡C bonds, and aromatic bonding (all of which involve  $p\pi \leftrightarrow p\pi$  bonding). This capability enables a larger number of reaction and compound types for carbon compared with silicon. Silicon can neither form molecules with comparably stable Si-Si bonds, nor form double or triple  $p\pi \leftrightarrow p\pi$  bonds. In general, silicon forms no divalent compounds although some unusual and usually unstable gas-phase compounds that are formally divalent are known. The gas-phase species singlet  $:\text{SiF}_2$  has a remarkably low reactivity and forms a polymeric low-temperature condensate (References 28 and 29).

Among the silicon compounds, only two (but large) classes have been identified as those that should receive consideration for development of fire suppression agents: the silanes that may contain Si-Si bonds (Figure 5), and the siloxanes that contain Si-O-Si linkages (Figure 6). All inorganic silicates are solids, and the silicon halides are highly susceptible to hydrolysis, rendering them toxic. Thus, these latter two families of compounds are not promising candidates as fire suppressants, though for different reasons.

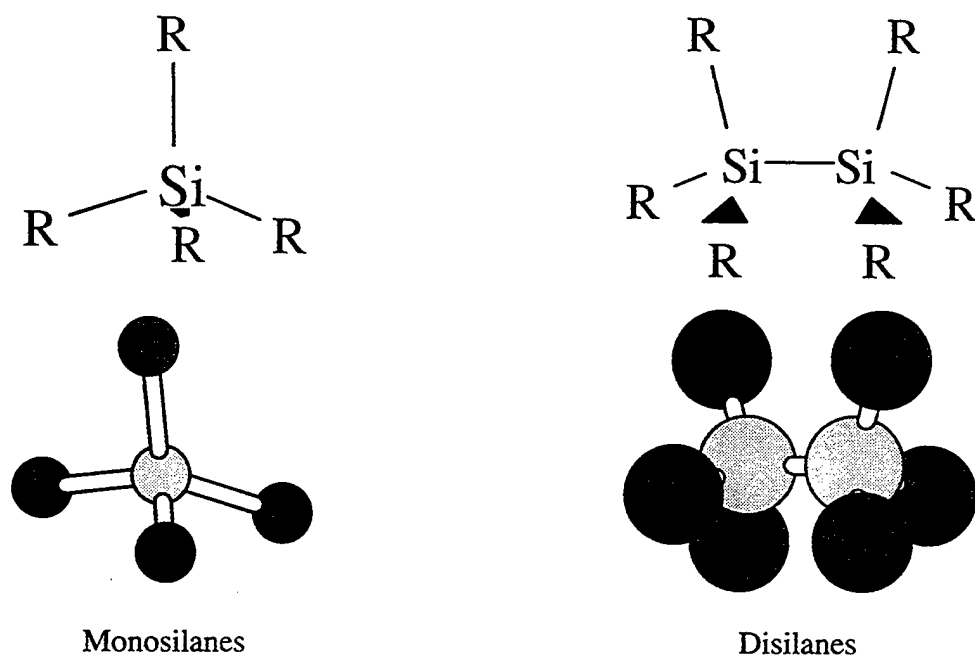


Figure 5. Silanes.

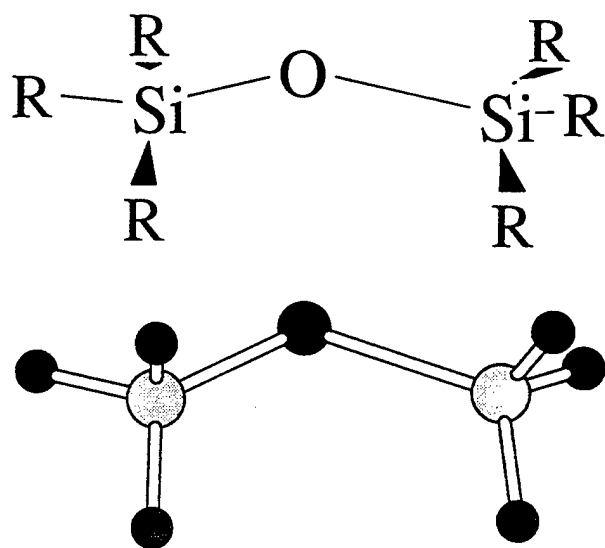


Figure 6. Siloxanes.

## SECTION V

### ENVIRONMENTAL PARAMETERS

Since environmental properties are of particular importance in determining the acceptability of chemical options to halons, the following contains a brief overview of the environmental properties of particular interest (Reference 1).

#### A. OZONE DEPLETION POTENTIAL

Ozone Depletion Potentials (ODP) are the calculated ozone depletions per unit mass of material released relative to a standard, normally CFC-11. It should be noted that ODPs are calculated; they cannot be measured. Calculations of ODPs require time horizons (see below); however, steady-state calculations are often used. Although ODPs vary somewhat depending on the calculation method, it is believed that relative values for compounds containing the same ozone-depleting element are relatively reliable. Thus, halocarbons that contain only chlorine and fluorine (in addition to carbon and, possibly, hydrogen) can be compared to CFC-11. It is well-established that bromine is much more damaging to ozone than is chlorine on a per atom basis. Exactly how much more, however, is not precisely known and lends some uncertainty to the ODPs of bromocarbons. An excellent nontechnical historical overview is contained in Reference 30.

#### B. ATMOSPHERIC LIFETIME

Atmospheric lifetimes are generally modeled as "e-folding" lifetimes. The gas concentration decays exponentially following Equation 1.

$$C_t = C_0 e^{-t/L} \quad [1]$$

where  $C_0$  is the initial concentration,  $C_t$  is the concentration at any time  $t$ , and  $L$  is the atmospheric lifetime. After one lifetime, the gas concentration drops to  $1/e$  (approximately 0.369) of its initial value. Note that this equation predicts that the concentration will never reach

zero, although it can approach it very closely. For example, after only five lifetimes, the concentration drops to 0.0067 of its initial value.

### C. GLOBAL WARMING POTENTIAL

The GWP is the calculated change in radiative forcing\* resulting from the emission of 1 kilogram of a chemical relative to the radiative forcing resulting from the emission of 1 kilogram of a reference gas. In the past, CFC-11 was often used as the reference; however, carbon dioxide is now typically used. The GWP depends on three variables: (1) the integrated infrared radiation absorption spectrum band strength, (2) the location of the IR absorption bands, and (3) the lifetime of the gas. It is important to note that the GWP can vary significantly depending on the time period used for the comparison of the radiative forcing of the chemical relative to that of the reference. The time period used to calculate the GWP is termed the "time horizon," and is primarily a policy decision. Time horizons of 100 and 500 years are often used in calculated GWP values; however, other time horizons may be more appropriate. GWPs with longer time periods are believed to be more inaccurate than those with shorter time periods (Reference 31).

Only a limited amount of information on estimated atmospheric lifetimes and GWPs of silicon compounds is available. Some information is presented in Table 5 (Reference 43). Insufficient details have been presented to allow judgment of the reliability of the values given. The value for  $\text{Si}(\text{CH}_3)_3\text{F}$  is suspect since one would expect this compound to undergo relatively rapid hydrolysis in the atmosphere (Reaction 13). Moreover, hydrolysis and, possibly, reaction with oxygen may be possible for the two hydrides ( $\text{CHF}_2\text{CF}_2\text{SiH}_3$  and  $\text{CF}_3\text{CH}_2\text{SiH}_3$ ). It may be that hydrolysis was not considered in obtaining these reported lifetimes.



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\*Radiative forcing is global atmospheric heating due to absorption and emission of radiation from the earth.



TABLE 5. ENVIRONMENTAL CHARACTERISTICS OF SOME SILANES.

Compound	Lifetime, years	GWP based on CFC-11	GWP based on carbon dioxide		
			20-year time horizon	100-year time horizon	500-year time horizon
$\text{Si}(\text{CH}_3)_3\text{CF}_3$	0.08	0.002	25	8	2
$\text{Si}(\text{CH}_3)_3\text{F}$	0.08	0.003	41	13	4
$\text{CHF}_2\text{CF}_2\text{SiH}_3$	0.44	0.01	156	48	15
$\text{CF}_3\text{CH}_2\text{SiH}_3$	0.44	0.01	170	52	16

In addition to this information, rate constants for reactions with tropospheric species for a series of low-molecular-weight methyl siloxanes (some of which are termed "volatile methyl siloxanes, VMSs" and are discussed further in the section on siloxanes in this report) have been determined (Reference 32). Reactions with nitrogen trioxide radical ( $\bullet\text{NO}_3$ ) and tropospheric ozone ( $\text{O}_3$ ) have been found to be negligible or of minor significance; however, reaction with tropospheric hydroxyl free radicals ( $\bullet\text{OH}$ ) are shown to provide an effective tropospheric removal mechanism (see Reference 33 for a discussion of removal mechanisms and rate constants). The second-order rate constants,  $k_1$ , for reaction of the low-molecular-weight disiloxanes (and tetramethylsilane) with  $\bullet\text{OH}$  are shown in Table 6. The atmospheric lifetimes in this table were calculated for an average tropospheric  $\bullet\text{OH}$  concentration  $[\bullet\text{OH}]$  of  $7.7 \times 10^{-5}$  molecules/cm<sup>3</sup>, although the actual concentration is likely to be slightly higher (giving an even shorter atmospheric lifetime).

TABLE 6. PARAMETERS FOR TROPOSPHERIC REMOVAL OF LOW-MOLECULAR-WEIGHT DISILOXANES AND TETRAMETHYLSILANE.

Compound	Second-order rate constant, $k_2$ , for reaction with $\bullet\text{OH}$ , $\text{cm}^3/\text{molecule-s}$	Atmospheric lifetime, days
$\text{Si}(\text{CH}_3)_4$	$1.00 \pm 0.27 \times 10^{-12}$	15
$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$	$1.38 \pm 0.012 \times 10^{-12}$	11
$[(\text{CH}_3)_2\text{SiO}]_3$	$5.2 \pm 1.7 \times 10^{-13}$	29
$[(\text{CH}_3)_2\text{SiO}]_4$	$1.01 \pm 0.32 \times 10^{-12}$	15
$[(\text{CH}_3)_2\text{SiO}]_5$	$1.55 \pm 0.49 \times 10^{-12}$	10

An estimation of the ODP for bromine-substituted silicon compounds can be made in two steps. First, we can estimate the change in atmospheric lifetime when a bromine atom is substituted for either a hydrogen atom or a fluorine atom in the silicon compounds in Table 5 or Table 6. Second, we can relate the atmospheric lifetimes for bromine-containing compounds to ODPs. The data required for the latter estimation are presented in Table 7.

A review of the data shown in Table 7 indicates that, excluding  $\text{CF}_4$  (which has an anomalously long lifetime), substitution of a fluorine atom with a bromine atom decreases the lifetime to values that range from 2.3 percent to 31.7 percent of the original value, with an average reduction (for 4 data points only) to 10 percent of the original value (i.e., a lifetime of 1/10 that of the compound without bromine substitution). This is probably due to the increased likelihood for tropospheric photolysis with the addition of bromine (Reference 33). Inclusion of  $\text{CF}_4$  in the compounds considered in Table 7 makes the decrease much larger.

The change in atmospheric lifetime accompanying substitution of a hydrogen atom with a bromine atom is less clearly defined. Table 7 shows that two such substitutions decreased the atmospheric lifetime (to 26 and 9 percent of the original value), while two others actually caused a small increase in lifetime (to 1.5 times the original value). The replacement of a hydrogen atom by a bromine atom decreases (or eliminates if only a single hydrogen atom is initially

TABLE 7. ATMOSPHERIC LIFETIMES AND ODPs.

Bromine-containing parent compounds			Replacement of one Br with one F		Replacement of one Br with one H	
Formula	Lifetime, years	ODP	Formula	Lifetime, years	Formula	Lifetime, years
CBrF <sub>2</sub> CBrF <sub>2</sub>	<sup>a</sup> 28	<sup>a</sup> 6.6	CF <sub>3</sub> CBrF <sub>2</sub>	--	CHF <sub>2</sub> CBrF <sub>2</sub>	--
CHBrF <sub>2</sub>	<sup>b</sup> 9	<sup>c</sup> 0.74	CHF <sub>3</sub>	<sup>d</sup> 250	CH <sub>2</sub> F <sub>2</sub>	<sup>d</sup> 6
CBrClF <sub>2</sub>	<sup>e</sup> 20	<sup>e</sup> 5.1	CClF <sub>3</sub>	<sup>d</sup> 640	CHClF <sub>2</sub>	<sup>d</sup> 13.3
CH <sub>3</sub> Br	<sup>e</sup> 1.3	<sup>e</sup> 0.64	CH <sub>3</sub> F	<sup>f</sup> 4.1	CH <sub>4</sub>	<sup>e</sup> 14.5
CBr <sub>2</sub> F <sub>2</sub>	<sup>a</sup> 1.5	<sup>a</sup> 0.3	CBrF <sub>3</sub>	<sup>d</sup> 65	CHBrClF	--
CBrF <sub>3</sub>	<sup>d</sup> 65	<sup>e</sup> 12	CF <sub>4</sub>	<sup>d</sup> 50000	CHF <sub>3</sub>	<sup>d</sup> 250

<sup>a</sup>Reference 34.<sup>b</sup>Reference 35.<sup>c</sup>Reference 36.<sup>d</sup>Reference 37.<sup>e</sup>Reference 38.<sup>f</sup>Reference 39.

present) the possibility for hydrogen atom abstraction by hydroxyl free radicals and increases the possibility for tropospheric photolysis (see Reference 33 for a discussion of tropospheric removal processes).

Thus, the limited data indicate that substitution of a fluorine atom by a bromine atom causes a decrease in atmospheric lifetime to approximately 1/10th of the original value. Such a decrease would give brominated derivatives of the silicon compounds shown in Table 5 atmospheric lifetimes on the order of a few days up to a month. On the other hand, Si(CH<sub>3</sub>)<sub>3</sub>CF<sub>3</sub> is the only compound in Table 5 that has a structure similar to those that are being considered in the work covered in this report. The other compounds contain Si-X or Si-H bonds, both of which are considered unsuitable for a candidate fire suppressant. However, Si(CH<sub>3</sub>)<sub>3</sub>CF<sub>3</sub> may have the most reliable atmospheric lifetime since it is not subject to hydrolysis or reaction with oxygen (see discussion above). Considering only the compound Si(CH<sub>3</sub>)<sub>3</sub>CF<sub>3</sub>, one arrives at a lifetime of approximately three days for the bromine-substituted derivative Si(CH<sub>3</sub>)<sub>3</sub>(CBrF<sub>2</sub>).

In the case of the compounds in Table 6, we can assume that substitution of a bromine for a hydrogen atom will not affect the atmospheric lifetime. However, such lifetimes are already short (10 to 30 days).

We can now estimate what this might mean. Plotting the ODP of bromocarbons as a function of atmospheric lifetime using data from Table 7 shows a nearly linear relationship (Figure 7). We have found that with HCFCs and CFCs, one needs to divide the ODP by the number of chlorine atoms to see any trend of increasing ODP with increasing atmospheric lifetime (Reference 33). That this is not necessary for the bromocarbons is probably due to a decrease in atmospheric lifetime as the number of bromine atoms is increased, which gives an increased probability of photolysis. The relatively few data points indicate a change in ODP of approximately 2 for each 10 years increase in atmospheric lifetime. For an atmospheric lifetime of 3 days (estimated for  $\text{Si}(\text{CH}_3)_3(\text{CBrF}_2)$ ), the estimated ODP is, therefore, 0.002. For an atmospheric lifetime of 30 days (the upper limit of those estimated for a bromine-substituted methylsiloxane), the ODP would be 0.02. Unlike HCFCs, which have other uses (for example, refrigeration, cleaning, and foam blowing) that cause an increased consumption and, therefore, an increased likelihood of regulation, brominated silicon compounds would be unlikely to have applications other than fire protection. Thus, with an ODP of 0.02 or below, it is unlikely that bromosilicon compounds would be significantly regulated. It is unfortunate that the only applicable reference compounds,  $\text{Si}(\text{CH}_3)_3\text{CF}_3$  and VMSs, contain many methyl groups and are, therefore, highly subject to reaction with hydroxyl free radicals. It is difficult to quantitatively determine what would occur were these methyl groups to be fully or partially fluorinated, but it is certain that the atmospheric lifetime would increase. Much more data on atmospheric lifetimes of silicon compounds are needed to make these estimates more reliable (or at least less suspect). Nevertheless, the exceedingly limited data available indicate that bromine-containing silicon compounds are likely to be environmentally acceptable.

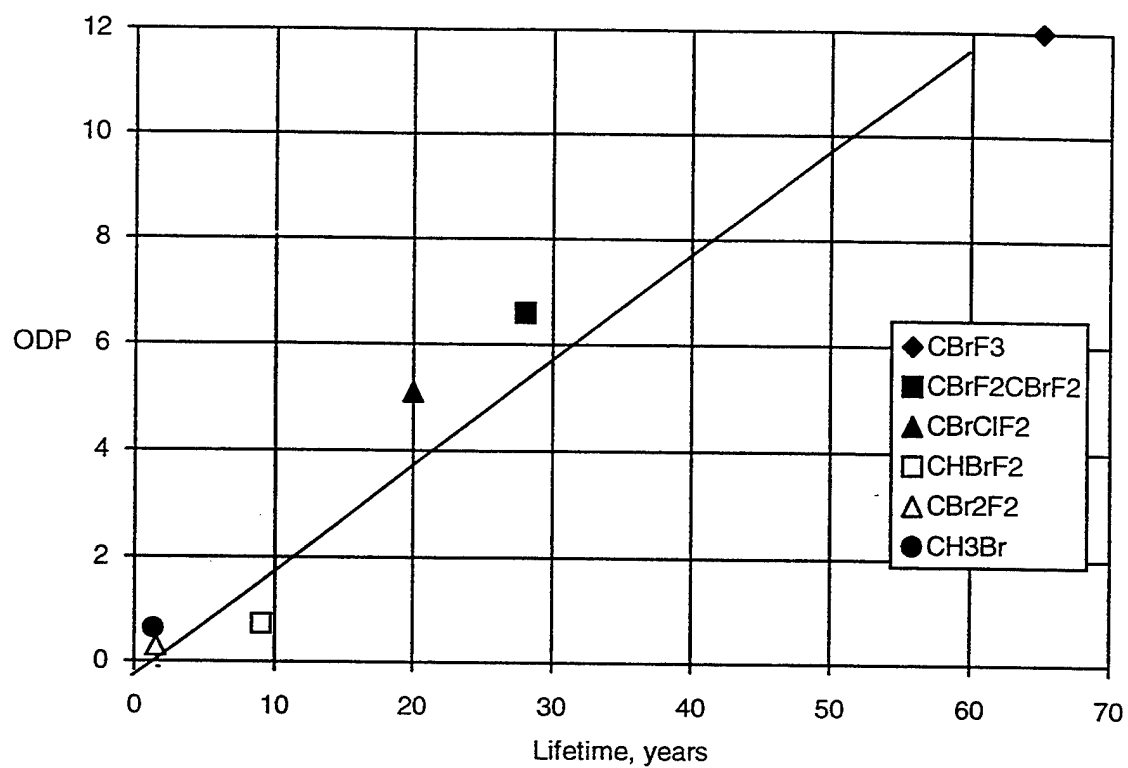


Figure 7. ODP as a Function of Atmospheric Lifetime for Bromocarbons.

## SECTION VI

### SILANES

#### A. HYDRIDES

Silanes are characterized by tetravalent silicon having no Si-O-Si linkages. The addition of  $\text{SiR}_2$  groups with Si-Si bonding gives linear or branched chains or cyclic rings (Figure 8). A good overview of cyclic structures is given in Reference 40.

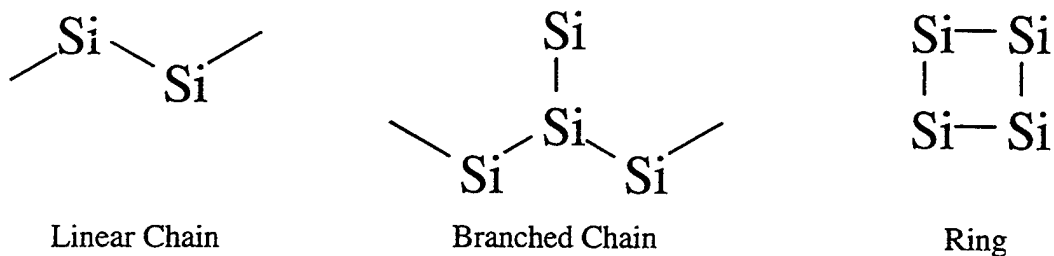


Figure 8. Silane Skeletons.

The simplest silane compounds are the hydrides, and the simplest hydride is  $\text{SiH}_4$  (monosilane or, simply, silane). The higher hydrides are  $\text{Si}_2\text{H}_6$  (disilane),  $\text{Si}_3\text{H}_8$  (trisilane),  $\text{Si}_4\text{H}_{10}$  (tetrasilane), etc. This homologous series bears structural resemblance to the alkane saturated hydrocarbons. The length of the silicon chain appears to be limited by an inherent instability that is unknown in carbon chains. Higher hydrides are unstable, and the largest member so far reported is hexasilane ( $\text{Si}_6\text{H}_{14}$ ).

In the absence of oxygen, monosilane is thermally quite stable and decomposes to silicon and hydrogen only at high temperatures. Higher silanes decompose at progressively lower temperatures. Disilane dissociates at 400 °C to 500 °C, and hexasilane decomposes completely at room temperature over several months. The higher hydrides do not break down to elemental

hydrogen and silicon, but undergo a series of complicated rearrangements resulting in mixtures of simple gaseous hydrides and solid unsaturated hydrides (e.g., Reaction 14).<sup>\*</sup> This spontaneous disproportionation of the higher hydrides explains why long chain silanes are not found.



Of greater importance, from the standpoint of possible use in synthesis, is the susceptibility of the hydrides to oxidation. Here, there is no marked differentiation. All the hydrides are extremely sensitive to oxygen and spontaneously ignite in air. The reaction proceeds with an explosive "puff," evidently because hydrogen is a preliminary product (Reaction 15). The hydrogen liberated by the initial oxidation forms an explosive mixture with oxygen, and this mixture is ignited by the rapidly rising temperature due to oxidation (Reaction 16; Reference 41)



The introduction of a chlorine atom or a methyl group into monosilane makes it no longer spontaneously flammable in air; however, the remaining hydrogen atoms can still be removed readily by mild oxidation, so that the substances are good reducing agents. In fact, any silicon-hydrogen bond may be expected to oxidize at elevated temperature in air, and at a rate far greater than that of the carbon hydrogen (C-H) bonds. Water will also oxidize the silicon-hydrogen bond in the presence of hydroxyl ion as a catalyst (Reaction 17; References 24 and 25).



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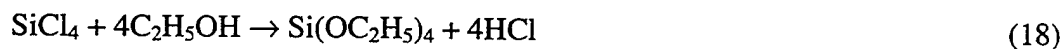
<sup>\*</sup>The "unsaturated hydrides," represented in this reaction as (SiH), are amorphous materials of uncertain composition probably containing silicon with interstitial hydrogen.

## B. HALOSILANES

Reactions of silicon with halogens are highly exothermic. The heat of formation of  $\text{SiCl}_4$  is -149 kJ/mol and that of  $\text{SiF}_4$  is -361 kJ/mol. This large negative enthalpy makes silicon halides the end products of many reactions involving halogens. For example, the reaction of HF with  $\text{SiO}_2$  gives  $\text{SiF}_4$ . This conversion of  $\text{SiO}_2$  to  $\text{SiF}_4$  liberates 80 kJ/mol, and the escape of the gaseous  $\text{SiF}_4$  drives the reaction to completion. The energy of the Si-X (X = F, Br, Cl, I) bond decreases and the reactivity increases with increasing atomic weight of the halogen (i.e., Si-Br is more reactive than Si-Cl or Si-F).

While the boiling points of the tetrafluorides of carbon and silicon (and also germanium and tin) increase with increasing atomic weight of the central atom, tetrachlorosilane and tetrabromosilane boil at lower temperatures than their carbon analogs (Table 8). This suggests that some intermolecular forces that are strong in tetrachloromethane and tetrabromomethane are reduced or absent in the corresponding silanes. The interaction may be of the  $p\pi \rightarrow d\pi$  type, between halogen atoms of different molecules. This would be insignificant in the fluorides because of the inaccessibility of the 3d orbitals of fluorine, but would be of importance in the heavier halides of carbon. In silicon halides, any intramolecular  $p\pi \rightarrow d\pi$  bonding between the central atom and the halogen make the p electrons of the halogens less available for intermolecular  $\pi$  bonding, leading to weaker intermolecular forces.

The Si-X bonds are stable in oxygen at room temperature. The silicon halides react with alcohols to form alkoxy derivatives (see below), which are volatile colorless liquids of pleasant odor (Reaction 18).



## C. ALKOXYSILANES AND ARYLOXYSILANES

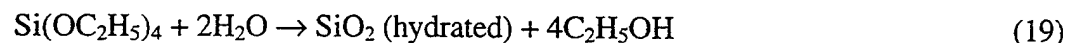
Alkoxysilanes and aryloxysilanes are often referred to as esters or organic orthosilicates since they are considered esters of the hypothetical orthosilicic acid ( $\text{Si}(\text{OH})_4$ ). Of particular interest to the user are the physiological reactions of the silicon esters with the human body.



TABLE 8. PHYSICAL PROPERTIES OF CARBON AND SILICON HALIDES.

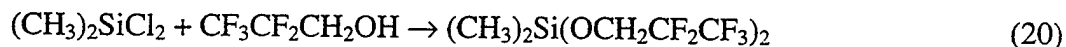
Compound	Bond energy, kJ/mol	Melting point, °C	Boiling point at 760 Torr, °C
SiF <sub>4</sub>	565	-90	-96
CF <sub>4</sub>	486	-185	-128
SiCl <sub>4</sub>	381	-70	57
CCl <sub>4</sub>	327	-23	76
SiBr <sub>4</sub>	310	5	155
CBr <sub>4</sub>	272	94	189-190
SiI <sub>4</sub>	234	124	290
Cl <sub>4</sub>	214	171	decomposes

Tetraethyl silicate (tetraethoxysilane, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) is readily absorbed and has a hemolytic effect (release of hemoglobin from red blood cells) such as that produced by ether, chloroform, or the higher alcohols. Hydrolysis, which releases ethyl alcohol, C<sub>2</sub>H<sub>5</sub>OH (Reaction 19), cannot account for the relatively high toxicity observed. Inhalation of air containing 9 to 20 mg/L or absorption of comparable quantities by other methods is fatal to experimental animals because of hemolysis. The gas phase concentration of 9 mg/L corresponds to less than 0.1 percent by volume. At lower concentration, no silicosis or any other unique effect attributable to the silicon content has been demonstrated (References 41 and 42).



Detailed properties of a number of fluoroalkoxy derivatives of silicon have been reported (Reference 43). It should be noted that there is a relationship between the fluorine content defined as  $N_F/(N_F + N_H)$ , where  $N_F$  is the number of fluorine atoms and  $N_H$  is the number of hydrogen atoms. As the fluorine content increases, the flash point increases (i.e., the flammability is reduced) until a nonflammable material is obtained. A similar trend is seen for other classes of compounds (Reference 43). All of the fluoroalkoxy compounds shown in Table 9 have an acute oral LD<sub>50</sub> of greater than 300 mg/kg (rat, 2 doses), exhibit a negative Ames

test for mutagenicity, and are non irritants to the skin (rabbit) (Reference 43). Note, however, that alkoxysilanes are often skin and eye irritants, sometimes severe. A typical preparation of these fluoroalkoxy compounds is shown in Reaction 20.



#### D. ORGANOSILANES

The simplest fully substituted alkyl and aryl silicon compounds have the formula  $\text{SiR}_4$ , where R is any hydrocarbon radical. The tetraalkylmonosilanes are stable to about 500 °C (Reference 44). The alkylidisilanes decompose above 450 °C, and the higher alkylsilanes decompose at successively lower temperatures. Tetramethylsilane is a colorless unreactive liquid of very little odor, boiling at 26 °C; tetraethylsilane boils at 154 °C (Reference 45). The ethyl groups may be chlorinated without breaking the C-Si bond, and if chlorine is in the *beta* position it may be removed as hydrogen chloride, leaving a vinyl group,  $-\text{CH}=\text{CH}_2$ , attached to silicon. Tetraphenylsilane crystallizes in colorless plates, melts at 233 °C, and boils above 530 °C (Reference 44).

Particular emphasis is due the organosilicon halides, specifically, the alkylhalosilanes, which are intermediates for silicone polymers. Their reactive halogen linkages allow ready conversion into silicols, alkoxysilanes, or siloxane polymers, which retain the organosilicon grouping present in the halide (References 25, 27, and 42).

A number of fluorinated tetramethylsilanes have been reported (Reference 46). The melting points can be compared with that of  $\text{Si}(\text{CH}_3)_4$ , at -91.1 °C. It should be noted that the two compounds containing trifluoromethyl ( $-\text{CF}_3$ ) groups have much lower melting points than the other compounds in Table 10.

TABLE 9. PROPERTIES OF SOME FLUOROALKOXY COMPOUNDS.

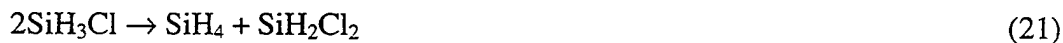
Compound	BP, 760 Torr, °C	Viscosity at 23 °C, cp	Liquid density, g/L	Surface tension at 23 °C, dynes/cm	Thermal conductivity , W/m-K	Specific heat, kJ/kg-K	Flash point, °C	Fluorine content, N <sub>F</sub> /(N <sub>F</sub> +N <sub>H</sub> )
Si(CH <sub>3</sub> ) <sub>3</sub> (OCH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> )	93.28	0.613	1.1021	15.20	0.0902	1.448	--	--
Si(CH <sub>3</sub> ) <sub>3</sub> [OCH(CF <sub>3</sub> ) <sub>2</sub> ]	89.43	0.687	1.1678	14.81	0.0796	1.411	--	--
Si(CH <sub>3</sub> ) <sub>2</sub> (OCH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	--	--	--	--	--	--	46	0.5
Si(CH <sub>3</sub> ) <sub>2</sub> [OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	--	--	--	--	--	--	none	0.75
Si(CH <sub>3</sub> )(OCH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub>	--	--	--	--	--	--	75	0.625

TABLE 10. FLUORINATED TETRAMETHYLSILANES.

Compound	Melting point, °C
Si(CH <sub>3</sub> ) <sub>3</sub> (CH <sub>2</sub> F)	-86.5 to -85.0
Si(CH <sub>3</sub> )(CH <sub>2</sub> F) <sub>3</sub>	-89.5 to -84.5
Si(CH <sub>3</sub> )CH <sub>2</sub> F) <sub>2</sub> (CHF <sub>2</sub> )	-63.5 to -62.0
Si(CH <sub>2</sub> F) <sub>4</sub>	-18.0 to -16.6
Si(CH <sub>3</sub> )(CH <sub>2</sub> F)(CHF <sub>2</sub> ) <sub>2</sub>	-58.7 to -56.8
Si(CH <sub>3</sub> )(CH <sub>2</sub> F) <sub>2</sub> (CF <sub>3</sub> )	-144 to -142.7
Si(CH <sub>2</sub> F) <sub>3</sub> (CHF <sub>2</sub> )	-54.0 to -53.2
Si(CH <sub>3</sub> )(CH <sub>2</sub> F)(CHF <sub>2</sub> )(CF <sub>3</sub> )	-144 to -138
Si(CH <sub>2</sub> F) <sub>2</sub> (CHF <sub>2</sub> ) <sub>2</sub>	-68.2 to -66.8
Si(CH <sub>2</sub> F)(CHF <sub>2</sub> ) <sub>3</sub>	-72.6 to -71

#### E. STABILITY

The reactivity of the Si-H bond toward oxygen is reduced if some of the hydrogen atoms bound to silicon are replaced by organic groups or by halogen atoms. The explosive or flammability limits of the methyl silanes at a given pressure increase as the number of methyl groups increases. Monosilane does not react with hydrocarbons at room temperature. At high temperatures or in the presence of a catalyst, silicon hydrides will react with a range of hydrocarbons. Almost all of the silicon halides containing two or three Si-H bonds show a tendency to disproportionate. Chlorosilane, for example, disproportionates to monosilane and dichlorosilane (Reaction 21). For most of these compounds, disproportionation is slow at room temperature, though the process is accelerated by almost any impurity. The derivatives of monosilane that are most liable to disproportionate in this way are the fluorides.



Silicon compounds containing fluoromethyl groups (-CH<sub>2</sub>F, -CHF<sub>2</sub>, and -CF<sub>3</sub>) are particularly unstable because they readily eliminate carbenes with formation of SiF bonds, as

seen in Reaction 22 (Reference 47). Compounds containing CHF moieties and direct silicon-chlorine bonds are dangerously shock-sensitive (Reference 48). For example,  $\text{Si}(\text{CHF}_2)_2\text{H}_2\text{Cl}$  can explode at or below room temperature (Reference 49). It is likely that this sensitivity extends to compounds containing CHF and silicon-bromine bonds.

In a series of compounds  $\text{Si}(\text{CF}_3)_n\text{X}_{4-n}$ , the stability decreases as the electronegativity of the halogen atom X and the number of groups increases (Reference 50). Thus,  $\text{Si}(\text{CF}_3)_4$  is reported to quantitatively decompose by carbene elimination at temperatures as low as 78 °C, compared with decomposition temperatures of 150 °C for  $\text{Si}(\text{CF}_2\text{HCF}_2)_4$  and 140 to 180 °C for  $\text{Si}(\text{CCl}_3)_4$  (Reference 51). It is interesting that the latter compound decomposes by transfer of a chlorine to the silicon to give  $\text{SiCl}_4$  and the carbene  $:\text{CCl}_2$ . Thus carbene elimination can occur with chlorocarbon substituents, as well as fluorocarbons.  $\text{Si}(\text{CF}_3)_2\text{H}_2\text{F}$  decomposes slowly at 110 °C, and  $\text{Si}(\text{CF}_3)_2\text{H}_2$  decomposes around 100 °C (Reference 50). On the other hand,  $\text{Si}(\text{CF}_3)_4$  is reported to be thermally stable up to 180 °C and not attacked by  $\text{O}_2$  and  $\text{H}_2\text{O}$  (Reference 52).



Silanes containing 1,1,2,2-tetrafluoroethyl groups ( $-\text{CF}_2\text{CHF}_2$ ) also decompose by  $\alpha$ -fluorine elimination. Thus,  $\text{Si}(\text{CF}_2\text{CHF}_2)_4$  thermally decomposes to give the  $:\text{CFCHF}_2$  carbene and  $\text{SiF}_4$  (Reference 53). 2,2-Difluoroethylsilicon compounds,  $\text{CHF}_2\text{CH}_2\text{-Si}$ , on the other hand, decompose by  $\beta$ -fluorine elimination (Reference 54).

## F. SILICON TO CARBON BONDS

Some of the physical properties of the tetramethyl derivatives of carbon and silicon are given in Table 11 (Reference 55). Tetraalkylsilanes are thermally stable up to 500 °C. The decomposition products include monosilane, indicating that C-H as well as Si-C bonds are broken during the process.

TABLE 11. PHYSICAL PROPERTIES OF TETRAMETHYL DERIVATIVES OF SILICON AND CARBON.

Compound	Formula	Bond energy	Melting point, °C	Boiling point at 760 Torr, °C
Si(CH <sub>3</sub> ) <sub>4</sub>	C <sub>4</sub> H <sub>12</sub> Si	310	-102	27
C(CH <sub>3</sub> ) <sub>4</sub>	C <sub>5</sub> H <sub>12</sub>	347	-16.5	9.5

Unsaturation ( $p\pi \leftrightarrow p\pi$  bonding) at carbon sites has a marked effect on the length and force constant of the methyl-carbon bond, through the change in hybridization at carbon. As noted earlier, such unsaturation is unknown for silicon compounds.

The silicon-carbon bond (Si-C) is surprisingly inert. Its bond energy is not very high, and is much less than the energies of the Si-O and Si-F bonds. Nevertheless, bonds from silicon to saturated aliphatic groups persist through a variety of chemical reactions, and are moderately stable to such strong reagents as alkali. The reason for this low reactivity undoubtedly involves activation energies, since many of the compounds are thermodynamically unstable to possible products. If the carbon atom bound to silicon is unsaturated, the Si-C bond is appreciably more reactive.

The Si-C bond is chemically similar to the H-C bond. Si-C bonds may be broken by electrophilic or nucleophilic attack. In general, substitution at silicon or at carbon makes the Si-C bond more easily broken.

#### G. SILICON-SILICON BOND

Silicon-silicon bonds are formed in the pyrolysis of monosilane and of tetraalkylsilanes, although there exist several other more efficient processes for their formation. Some of the physical properties of the C<sub>2</sub>H<sub>6</sub> (ethane) and Si<sub>2</sub>H<sub>6</sub> (disilane) are given in Table 12 (Reference 26).

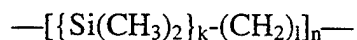
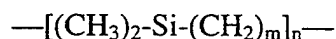
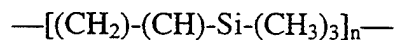
TABLE 12. PROPERTIES OF THE 2-CARBON AND 2-SILICON HYDRIDES.

Compound	C-C or Si-Si Bond energy	Melting point, °C	Boiling point at 760 Torr, °C
Si <sub>2</sub> H <sub>6</sub>	214	-132	-15
C <sub>2</sub> H <sub>6</sub>	347	-183	-89

With oxygen the higher silicon hydrides react violently and are completely oxidized to silica and water. Hexaalkyldisilanes, on the other hand, are relatively inert towards oxygen. This is an activation energy effect since oxidation is thermodynamically possible. It is not easy to separate the activities towards oxygen of the Si-Si and the Si-H bonds in the higher hydrides; the first step in the oxidation is probably the attack at one of the Si-H bonds. The Si-Si bond is broken only slowly by water but aqueous alkali reacts quantitatively with Si-Si bonds to give hydrogen. Polysilanes are of current importance as photoresists and as precursors to new polycarbosilane polymers.

#### H. POLYSILAHYDROCARBONS

Linear heterochain silahydrocarbons not containing silicon-silicon bonds in the main chain are used as bricks to build up oxygen-free organosilicon polymeric materials known as polysilahydrocarbons (PSHC). Depending on the structure of their main chain, one may divide PHSC into four types:



These compounds are universally membranes and/or resins with very useful permeability properties. Thus, the absence of hydrogen bonds and/or oxygen bonds leads to a non-volatile end result that rules these compounds out as fire suppressants (see Reference 56 for details).

## I. SURVEY OF SILANES

A survey of silanes was performed using information from References 12, 27, 41, 42, 49, 50, 55, and 57-68. The compounds found were divided into two groups—those containing organofluorine and organobromine substituents (of primary interest here) and other silicon compounds that provide a general overview of silicon chemistry. The latter compounds are listed in Table 13 and the remainder are discussed in the following section. The list in Table 13 is by no means comprehensive and is meant to give a general overview of the types of silanes available. One of the most notable features is that many of the silanes in Table 13 are highly reactive. The materials are often corrosive, and/or flammable, etc. (Where a note for a compound is blank, it has been possible to gather information on the existence and synthesis of a compound, but no information on the physical properties of that compound relative to handling or safety was immediately available from the primary literature source.) On the other hand, it must be recognized that most of the compounds contain Si-X bonds, and such compounds are known to be corrosive and toxic.

Although Si-X bonds readily hydrolyze to give the H-halogen products, and silanes having Si-H bonds are highly reactive, these compounds were included to give some indication of how the physical properties vary and to provide an overview of compounds that might be useful in syntheses.

## J. SILANES WITH BROMOCARBON AND FLUOROCARBON GROUPS

Silanes containing organobromine and organofluorine substituents were separated from the initial list and are discussed in this section. Table 14 and Table 15 contain lists of all of the substituents found with the exception of those containing metals, sulfur, and phosphorus, and with the exception of highly active groups (such as bromoketene). Each different substituent has been assigned a label ("Bn" in the case of the organobromine substituent groups and "An" in the case of the organofluorine substituents, where "n" is an arbitrary number) to make the identification of compounds containing the substituent easier and to simplify the structural formulas to better compare compounds. Some silanes containing each substituent are shown in



TABLE 13. SILANES AND SILANOLS.

Empirical formula	Structural formula	Name	MP, °C	BP, °C	Notes <sup>b</sup>
BrF <sub>3</sub> Si	SiBrF <sub>3</sub>	bromotrifluorosilane		-42	CAS No. 14049-39-9, M, G, C, T
Br <sub>3</sub> FSi	SiBr <sub>3</sub> F	tribromofluorosilane		84	CAS No. 18356-67-7, M, L, C, T
Br <sub>4</sub> Si	SiBr <sub>4</sub>	tetrabromosilane	5	153	M, L, C, T, no flash point
Cl <sub>3</sub> FSi	SiCl <sub>3</sub> F	trichlorofluorosilane		15	CAS No. 14965-52-77, M, G, C, T
Cl <sub>4</sub> Si	SiCl <sub>4</sub>	tetrachlorosilane		58	CAS No. 10026-04-07, M, L, C, T
F <sub>4</sub> Si	SiF <sub>4</sub>	tetrafluorosilane	-90	-65	CAS No. 7783-61-1, M, G, C, T, nonflamm.
I <sub>4</sub> Si	SiI <sub>4</sub>	tetraiodosilane	124	290	
H <sub>6</sub> Si <sub>2</sub>	Si <sub>2</sub> H <sub>6</sub>	disilane			
H <sub>14</sub> Si <sub>6</sub>	Si <sub>6</sub> H <sub>14</sub>	hexasilane			

TABLE 13. SILANES AND SILANOLS (continued).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
CH <sub>2</sub> Cl <sub>4</sub> Si	Si(CH <sub>2</sub> Cl)Cl <sub>3</sub>	(chloromethyl)trichlorosilane	---	---	T, C
CH <sub>3</sub> Br <sub>3</sub> Si	Si(CH <sub>3</sub> )Br <sub>3</sub>	methyltribromosilane	-28	132	
CH <sub>3</sub> Cl <sub>3</sub> Si	Si(CH <sub>3</sub> )Cl <sub>3</sub>	methyltrichlorosilane	---	66	CAS No. 75-96-6, T, C, F, L
CH <sub>4</sub> Cl <sub>2</sub> Si	Si(CH <sub>3</sub> )HCl <sub>2</sub>	methyldichlorosilane	-93	41	L, F, C
CH <sub>5</sub> ClSi	Si(CH <sub>3</sub> )H <sub>2</sub> Cl	chloromethylsilane	-135	7	
CH <sub>5</sub> Cl <sub>3</sub> Si <sub>2</sub>	SiH <sub>2</sub> (CCl <sub>3</sub> )SiH <sub>3</sub>	(trichloromethyl)disilane	---	---	
CH <sub>6</sub> Si	Si(CH <sub>3</sub> )H <sub>3</sub>	methylsilane	-157	-57	
C <sub>2</sub> H <sub>2</sub> Cl <sub>6</sub> Si <sub>2</sub>	CH <sub>2</sub> =C(SiCl <sub>3</sub> ) <sub>2</sub>	ethenylbis(trichlorosilane)	---	---	
C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub> Si	CH <sub>2</sub> =CHSiCl <sub>3</sub>	trichlorovinylsilane	-95	90	F, C
CH <sub>3</sub> Cl <sub>5</sub> Si <sub>2</sub>	Si(CH <sub>3</sub> )Cl <sub>2</sub> SiCl <sub>3</sub>	pentachloromethyldisilane	---	---	
C <sub>2</sub> H <sub>4</sub> F <sub>6</sub> Si <sub>2</sub>	SiF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SiF <sub>3</sub>	1,2-ethanediylbis(trifluorosilane)			
C <sub>2</sub> H <sub>5</sub> ClSi	Si(CH <sub>3</sub> ) <sub>3</sub> (CH <sub>2</sub> Cl)	(chloromethyl)trimethylsilane		98	CAS No. 2344-80-1, L, T
C <sub>2</sub> H <sub>5</sub> Cl <sub>3</sub> Si	Si(CH <sub>3</sub> )(CH <sub>2</sub> Cl)Cl <sub>2</sub>	dichloro(chloromethyl)methylsilane	---	121	F, C
C <sub>2</sub> H <sub>5</sub> Cl <sub>3</sub> Si	Si(C <sub>2</sub> H <sub>5</sub> )Cl <sub>3</sub>	trichloro(ethyl)silane	-106	99	F, C
C <sub>2</sub> H <sub>5</sub> F <sub>3</sub> OSi	Si(OC <sub>2</sub> H <sub>5</sub> )F <sub>3</sub>	ethoxytrifluorosilane	-122	-7	
C <sub>2</sub> H <sub>6</sub> Br <sub>2</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub>	dibromodimethylsilane	-58	112	

TABLE 13. SILANES AND SILANOLS (continued).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
C <sub>2</sub> H <sub>6</sub> Cl <sub>2</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	dichlorodimethylsilane	-76	7-	T, F
C <sub>2</sub> H <sub>6</sub> Cl <sub>4</sub> Si <sub>2</sub>	Si(CH <sub>3</sub> )Cl <sub>2</sub> Si(CH <sub>3</sub> )Cl <sub>2</sub>	1,1,2,2-tetrachloro-1,2-dimethyldisilane	--	--	C, F, flash point = 49 °C
C <sub>2</sub> H <sub>7</sub> ClSi	Si(CH <sub>3</sub> ) <sub>3</sub> HCl	chlorodimethylsilane	-111	35	L, F, C
C <sub>3</sub> H <sub>7</sub> Cl <sub>3</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> (CHCl <sub>2</sub> )Cl	chloro(dichloromethyl)dimethylsilane	-48	149	
C <sub>3</sub> H <sub>8</sub> Cl <sub>2</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Cl)Cl	chloro(chloromethyl)dimethylsilane	---	114	L, F, M
C <sub>3</sub> H <sub>9</sub> BrSi	Si(CH <sub>3</sub> ) <sub>3</sub> Br	bromotrimethylsilane	-43	79	L, F, C, flash point = 90 °C
C <sub>3</sub> H <sub>9</sub> ClO <sub>3</sub> Si	Si(OCH <sub>3</sub> ) <sub>3</sub> Cl	chlorotrimethoxysilane	---	112	L, F, C
C <sub>3</sub> H <sub>9</sub> ClSi	Si(CH <sub>3</sub> ) <sub>3</sub> Cl	chlorotrimethylsilane	-40	57	CAS No. 75-77-4, T, C, F, flash-point = 27 °C
C <sub>3</sub> H <sub>9</sub> FSi	Si(CH <sub>3</sub> ) <sub>3</sub> F	fluorotrimethylsilane	-74	16	G, F, C, flash point = -30 °C
C <sub>3</sub> H <sub>9</sub> ISi	Si(CH <sub>3</sub> ) <sub>3</sub> I	iodotrimethylsilane	---	106	L, F, C
C <sub>3</sub> H <sub>10</sub> OSi	Si(OCH <sub>3</sub> ) <sub>3</sub> H	trimethoxysilane	-115	81	L, F, C, T
C <sub>3</sub> H <sub>10</sub> Si	Si(CH <sub>3</sub> ) <sub>3</sub> H	trimethylsilane	-136	7	
C <sub>4</sub> H <sub>6</sub> Cl <sub>3</sub> NSi	(SiCl <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C≡N	4-(trichlorosilyl)butyronitrile	---	237	C, M

TABLE 13. SILANES AND SILANOLS (continued).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
C <sub>4</sub> H <sub>9</sub> ClSi	CH <sub>2</sub> =CHSi(CH <sub>3</sub> ) <sub>2</sub> Cl	chlorodimethylvinylsilane	--	82	L, F, C
C <sub>4</sub> H <sub>9</sub> Cl <sub>3</sub> Si	Si(C <sub>4</sub> H <sub>9</sub> )Cl <sub>3</sub>	butyltrichlorosilane	--	149	C
C <sub>4</sub> H <sub>9</sub> Cl <sub>3</sub> Si	Si(CH <sub>3</sub> ) <sub>3</sub> (CCl <sub>3</sub> )	(trichloromethyl)trimethylsilane	129	--	
C <sub>4</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>2</sub> Si	Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	dichlorodiethoxysilane	--	85	F, C, flash point = 31 °C
C <sub>4</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>3</sub> Si	Si(OCH <sub>3</sub> ) <sub>3</sub> (CHCl <sub>2</sub> )	(dichloromethyl)trimethoxysilane	--	--	
C <sub>4</sub> H <sub>10</sub> Cl <sub>2</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Cl) <sub>2</sub>	bis(chloromethyl)dimethylsilane	--	160	C, F, CAS No. 2917-46-6
C <sub>4</sub> H <sub>10</sub> Cl <sub>2</sub> Si	Si(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub>	dichlorodiethylsilane	--	128	L, F, C
C <sub>4</sub> H <sub>10</sub> Cl <sub>4</sub> Si <sub>2</sub>	Si(CH <sub>3</sub> ) <sub>2</sub> [CHSiCl <sub>3</sub> CH <sub>3</sub> ]Cl	chlorodimethyl[1-(trichlorosilyl)ethyl]silane	--	--	
C <sub>4</sub> H <sub>11</sub> ClOSi	Si(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> Cl)OH	(2-chloroethyl)dimethylsilanol	--	--	
C <sub>4</sub> H <sub>11</sub> ClO <sub>2</sub> Si	Si(CH <sub>3</sub> )(OCH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Cl)	(chloromethyl)dimethoxymethylsilane	--	--	
C <sub>4</sub> H <sub>11</sub> ClO <sub>3</sub> Si	Si(CH <sub>3</sub> )(OCH <sub>3</sub> ) <sub>3</sub>	(chloromethyl)trimethoxysilane	--	--	
C <sub>4</sub> H <sub>11</sub> ClSi	Si(CH <sub>3</sub> ) <sub>3</sub> (CH <sub>2</sub> Cl)	(chloromethyl)trimethylsilane	--	199	
C <sub>4</sub> H <sub>11</sub> ClSi	Si(CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )Cl	chlorodimethylethylsilane	--	89	L, F, C
C <sub>4</sub> H <sub>11</sub> ISi	Si(CH <sub>3</sub> ) <sub>3</sub> (CH <sub>2</sub> I)	(iodomethyl)trimethylsilane	--	140	L, F, C
C <sub>4</sub> H <sub>12</sub> O <sub>2</sub> Si	Si(CH <sub>3</sub> ) <sub>3</sub> (OCH <sub>3</sub> )	methoxytrimethylsilane	--	57	L, F, M

TABLE 13. SILANES AND SILANOLS (continued).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
C <sub>4</sub> H <sub>12</sub> Si	Si(CH <sub>3</sub> ) <sub>4</sub>	tetramethylsilane	-99	27	CAS No. 75-76-3, L, F, T, hygroscopic
C <sub>4</sub> H <sub>16</sub> Cl <sub>2</sub> Si <sub>2</sub>	Si <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (CH <sub>2</sub> Cl) <sub>2</sub>	bis(chloromethyl)tetramethyldisilane	---	---	
C <sub>4</sub> H <sub>20</sub> O <sub>4</sub> Si	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	tetraethoxysilane	110	168.1	L, M, T, F
C <sub>5</sub> H <sub>11</sub> Cl <sub>3</sub> Si	Si(C <sub>3</sub> H <sub>7</sub> )Cl <sub>3</sub>	pentyltrichlorosilane	---	---	L, F, C
C <sub>6</sub> H <sub>8</sub> Si	Si(C <sub>6</sub> H <sub>5</sub> )H <sub>3</sub>	phenylsilane	---	20	L, F, I
C <sub>6</sub> H <sub>10</sub> O <sub>2</sub> Si	Si(CH <sub>3</sub> ) <sub>3</sub> (OOC≡CH)	trimethylsilylpropynoate	---	---	L, F, M
C <sub>6</sub> H <sub>11</sub> Cl <sub>3</sub> Si	Si(C <sub>6</sub> H <sub>11</sub> )Cl <sub>3</sub>	cyclohexyltrichlorosilane	---	81	T, C
C <sub>6</sub> H <sub>12</sub> OSi	Si(CH <sub>3</sub> ) <sub>3</sub> (OCH <sub>2</sub> C≡CH)	propargyloxytrimethylsilane	---	52	L, F, I
C <sub>6</sub> H <sub>13</sub> ClSi	Si(CH <sub>3</sub> ) <sub>3</sub> (CH <sub>2</sub> CH=CHCl)	(3-chloroallyl)trimethylsilane	---	137	L, F, C
C <sub>6</sub> H <sub>14</sub> Cl <sub>2</sub> Si <sub>2</sub>	Si(CH <sub>3</sub> ) <sub>3</sub> [CH=CH(Si(CH <sub>3</sub> )Cl <sub>2</sub> )]	[2-(dichloromethylsilyl)ethenyl]-trimethylsilane	---	---	
C <sub>6</sub> H <sub>14</sub> OSi	Si(CH <sub>3</sub> ) <sub>3</sub> (OCH <sub>2</sub> CH=CH <sub>2</sub> )	allyloxytrimethylsilane	---	100	L, F, M
C <sub>6</sub> H <sub>14</sub> OSi	Si(CH <sub>3</sub> ) <sub>3</sub> [O(CH <sub>3</sub> )C=CH <sub>2</sub> ]	trimethyl(2-propenyloxy)silane	---	---	F, I, flash point = 7 °C
C <sub>6</sub> H <sub>14</sub> Si	Si(CH <sub>3</sub> ) <sub>3</sub> (CH <sub>2</sub> CH=CH <sub>2</sub> )	allyltrimethylsilane	---	86	L, F, I
C <sub>6</sub> H <sub>15</sub> ClOSi	Si(CH <sub>3</sub> ) <sub>3</sub> (OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl)	(3-chloropropoxy)trimethylsilane	---	---	

TABLE 13. SILANES AND SILANOLS (continued).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
C <sub>6</sub> H <sub>15</sub> ClOSi	Si(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Cl)[OCH(CH <sub>3</sub> ) <sub>2</sub> ]	chloromethyl(dimethylisopropoxysilane	---	64	L, F, I, Flash = 28
C <sub>6</sub> H <sub>15</sub> ClO <sub>2</sub> Si	Si(CH <sub>3</sub> )(CH <sub>2</sub> Cl)(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	(chloromethyl)diethoxymethylsilane	---	161	M, oral rat LD <sub>50</sub> = 1300mg/kg
C <sub>6</sub> H <sub>15</sub> ClO <sub>2</sub> Si	Si(CH <sub>3</sub> )(OCH <sub>3</sub> ) <sub>2</sub> [CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl]	(3-chloropropyl)dimethoxymethylsilane	---	168	F, I, flash point = 46 °C
C <sub>6</sub> H <sub>15</sub> ClO <sub>3</sub> Si	Si(OCH <sub>3</sub> ) <sub>3</sub> [CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl]	(3-chloropropyl)trimethoxysilane	---	156	F, C, flash point = 47 °C
C <sub>6</sub> H <sub>16</sub> F <sub>2</sub> Si <sub>2</sub>	SiF(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiF(CH <sub>3</sub> ) <sub>2</sub>	1,2-ethanediylbis(fluorodimethylsilane)	---	---	
C <sub>6</sub> H <sub>16</sub> OSi	Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> OH	triethylsilanol	---	158	
C <sub>6</sub> H <sub>16</sub> O <sub>2</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	diethoxydimethylsilane	---	114	CAS No. 2553-19-76, F, I, flash point = 11 °C
C <sub>6</sub> H <sub>16</sub> O <sub>3</sub> Si	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> H	triethoxysilane	---	134	L, T, F
C <sub>6</sub> H <sub>16</sub> O <sub>3</sub> Si	Si(OCH <sub>3</sub> ) <sub>3</sub> (C <sub>3</sub> H <sub>7</sub> )	trimethoxypropylsilane	---	142	I, M
C <sub>6</sub> H <sub>18</sub> Si <sub>2</sub>	Si(CH <sub>3</sub> ) <sub>3</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	hexamethyldisilane	---	113	L, F, I
C <sub>7</sub> H <sub>8</sub> Cl <sub>2</sub> Si	Si(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )Cl <sub>2</sub>	dichloromethylphenylsilane	---	205	C, M
C <sub>7</sub> H <sub>12</sub> O <sub>6</sub> Si	Si(CH <sub>3</sub> )(OOCCH <sub>3</sub> ) <sub>3</sub>	methyltriacetoxysilane	42	94	M

TABLE 13. SILANES AND SILANOLS (concluded).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
C <sub>7</sub> H <sub>16</sub> O <sub>2</sub> Si	Si(CH <sub>3</sub> )(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (CH=CH <sub>2</sub> )	diethoxymethylvinylsilane	---	133	L, F, M
C <sub>7</sub> H <sub>18</sub> O <sub>3</sub> Si	Si(OCH <sub>3</sub> ) <sub>3</sub> [CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ]	iso-butyltrimethoxysilane	---	154	I, M
C <sub>8</sub> H <sub>11</sub> Cl <sub>3</sub> Si <sub>2</sub>	Si(C <sub>8</sub> H <sub>11</sub> )Cl <sub>3</sub>	bicyclo(4.2.0)oct-1(6)-en-3-yltrichlorosilane	---	81(10)	T, C
C <sub>8</sub> H <sub>16</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	diallyldimethylsilane	---	54(70)	L, F, I
C <sub>8</sub> H <sub>17</sub> ClSi	Si(CH <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>11</sub> )Cl	chloro(cyclohexyl)dimethylsilane	---	96(40)	C, M, flash point = 62 °C
C <sub>8</sub> H <sub>18</sub> Cl <sub>2</sub> Si	Si[C(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> Cl <sub>2</sub>	di- <i>t</i> -butyldichlorosilane	-15	190	C, I, flash point = 61 °C
C <sub>8</sub> H <sub>18</sub> O <sub>3</sub> Si	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (CH=CH <sub>2</sub> )	triethoxyvinylsilane	---	160	L, F, M, flash point = 34 °C
C <sub>8</sub> H <sub>18</sub> Si	Si(CH <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>11</sub> )H	cyclohexyldimethylsilane	---	81(10)	L, F, I, flash point = 31 °C
C <sub>12</sub> H <sub>10</sub> Cl <sub>2</sub> Si	Si(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Cl	dichlorodiphenylsilane	--	305	C, M

<sup>a</sup>Boiling points are at 1 atmosphere (760 Torr) except where values in parentheses give the pressure (in Torr).<sup>b</sup>G = gas, I = irritant, L = liquid, S = solid, M = moisture sensitive, T = toxic, F = flammable, C = corrosive.

TABLE 14. ORGANOCHLORINE GROUPS IN SILANES.

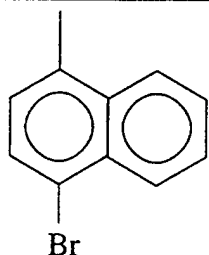
Group label	Structural formula	CAS No. of parent compound
B1		102246-26-4
B2	-CH <sub>2</sub> Br	62978-02-3 17760-18-8 7570-21-0 106916-82-9 16532-02-8 18243-41-9
B3	-CHBrCH <sub>2</sub> Br	4170-50-7 18146-08-2
B4	-CHBrCl	
B5	-CH <sub>2</sub> CH <sub>2</sub> Br	18156-67-7
B6	-CH=CHBr ( <i>trans</i> )	41309-43-7
B7	-C≡CCH <sub>2</sub> Br	38002-45-8
B8	-CH <sub>2</sub> CBr=CH <sub>2</sub>	
B9	-OCH=CBrCH <sub>2</sub> CH <sub>3</sub>	
B10	-CBr <sub>3</sub>	18142-75-1
B11	-CHBr <sub>2</sub>	2612-42-2
B12	-C≡CBr	18243-59-9 38177-63-8
B13	-CHBr=CH <sub>2</sub>	13683-41-5 18676-45-4
B14	-CH <sub>2</sub> CHBrCH <sub>3</sub>	
B15	-CBr <sub>2</sub> -	29955-10-0



TABLE 14. ORGANOBROMINE GROUPS IN SILANES (continued).

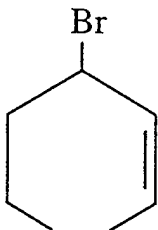
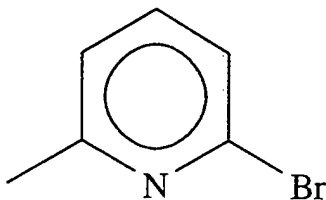
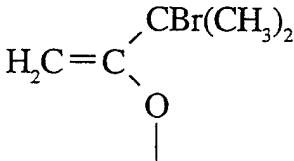
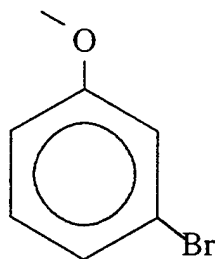
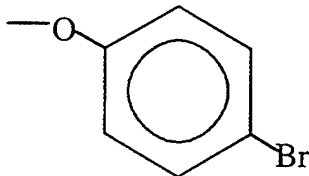
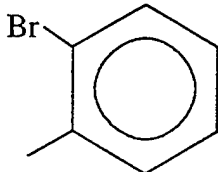
Group label	Structural formula	CAS No. of parent compound
B16		
B17		59409-80-2
B18		69278-36-0
B19		36971-28-5
B20		17878-44-3
B21		17878-37-4

TABLE 14. ORGANOCHLORINE GROUPS IN SILANES (continued).

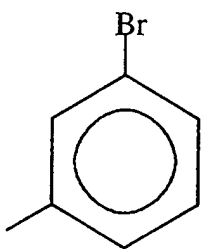
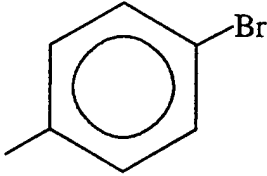
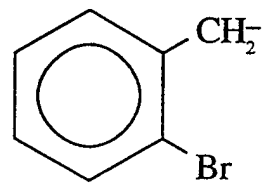
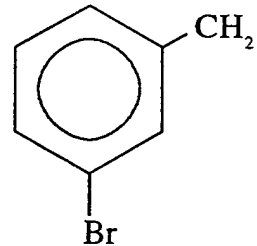
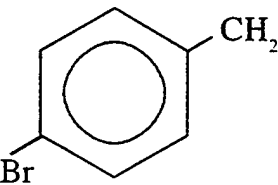
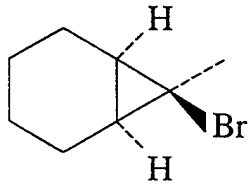
Group label	Structural formula	CAS No. of parent compound
B22		17878-47-6
B23		6999-03-7
B24	$\text{-C}\equiv\text{CC}\equiv\text{CBr}$	55552-44-8
B25		
B26		1833-43-8
B27		17095-20-4
B28		43131-20-0

TABLE 14. ORGANOBROMINE GROUPS IN SILANES (concluded).

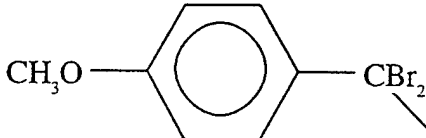
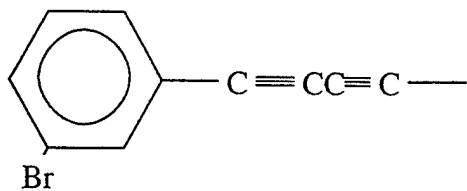
Group label	Structural formula	CAS No. of parent compound
B29		76943-81-2
B30		32117-60-50
B31	$-\text{C}(\text{CH}_3)=\text{CHBr}$	61979-41-7
B32	$-\text{CHBrF}$	
B33	$-\text{CBr}_2\text{F}$	
B34	$-\text{CBrF}_2$	

TABLE 15. ORGANOFLUORINE GROUPS IN SILANES.

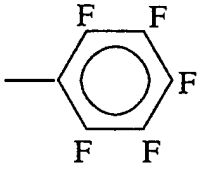
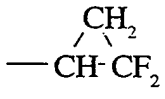
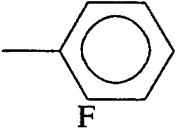
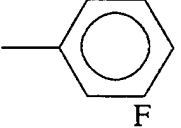
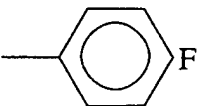
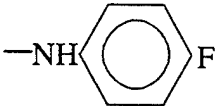
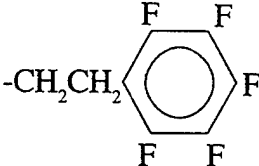
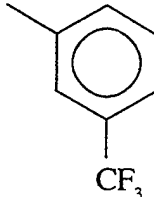
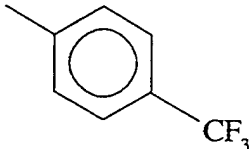
Group label	Structural formula	CAS No. of parent compound
A1	$-\text{CF}_2\text{CHF}_2$	4168-07-4
A2	$-\text{CH}_2\text{CF}_3$	
A3	$-\text{CF}_3$	
A4	$-\text{CHClF}$	
A5	$-\text{CH}_2\text{F}$	28871-61-6
A6	$-\text{OCH}_2\text{CF}_2\text{CF}_3$	
A7		5272-26-4 20160-40-1
A8	$-\text{OCH}_2(\text{CF}_3)_2$	
A9	$-\text{CH}_2\text{CH}_2\text{N}(\text{CF}_3)_2$	28871-58-1
A10	$-\text{CHF}_2$	
A11		
A12	$-\text{CH}_2\text{CH}_2\text{CF}_3$	675-62-7
A13	$-\text{OC}(\text{O})\text{CF}_3$	400-53-3
A14	$>\text{NC}(\text{CO})\text{CF}_3$	21149-38-2
A15	$-\text{N}=\text{C}(\text{CF}_3)-$	25561-30-2
A16		1842-26-8
A17		7217-41-6 20240-78-2
A18		455-17-4 1691-36-7

TABLE 15. ORGANOFLUORINE GROUPS IN SILANES (concluded).

Group label	Structural formula	CAS No. of parent compound
A19		33407-00-0
A20		35943-75-0
A21		386-92-5
A22		386-96-9
<sup>a</sup> A23	-OCH <sub>2</sub> CF <sub>3</sub>	

<sup>a</sup> Known as a substituent in siloxanes, as discussed further on in this report.

Table 16 and Table 17. The references in these two tables, for the most part, provide synthetic information.

The data collected show that there are very few silicon compounds containing fluoroorganic or bromoorganic groups. Most of the organobromine groups are large, bulky, and highly hydrogenated. The bromine-containing substituents of primary interest are -CH<sub>2</sub>Br (B2), -CHBrCl (B4), -CHBr<sub>2</sub> (B11), -CHBrF (B32), -CFBr<sub>2</sub> (B33), and, possibly, -CBr<sub>3</sub> (B10). There are even fewer compounds of silicon with organofluorine substituents.

TABLE 16. SELECTED SILANES WITH ORGANOCHLORINE GROUPS.

Empirical formula	Structural formula	Name	Ref	CAS No.
$\text{CH}_2\text{BrCl}_3\text{Si}$	$\text{Si}(\text{B}2)\text{Cl}_3$	(bromomethyl)trichlorosilane	69	17760-18-8
$\text{CH}_3\text{BrSi}$	$\text{Si}(\text{B}2)\text{H}_3$	(bromomethyl)silane	70	7570-21-0
$\text{C}_2\text{H}_3\text{Br}_2\text{Cl}_3\text{Si}$	$\text{Si}(\text{B}3)\text{Cl}_3$	trichloro(1,2-dibromoethyl)silane	71	4170-50-7
$\text{C}_3\text{H}_8\text{BrClSi}$	$\text{Si}(\text{B}2)(\text{CH}_3)_2\text{Cl}$	(bromomethyl)chlorodimethylsilane [BP = 133-135 °C, flash point = 41 °C]	72	16532-02-8
$\text{C}_4\text{H}_9\text{BrF}_2\text{Si}$	$\text{Si}(\text{B}34)(\text{CH}_3)_3$	trimethyl(bromodifluoromethyl)silane		
$\text{C}_4\text{H}_9\text{Br}_3\text{Si}$	$\text{Si}(\text{B}10)(\text{CH}_3)_3$	trimethyl(tribromomethyl)silane [MP = 203-205 °C]	73	18142-75-1
$\text{C}_4\text{H}_{10}\text{BrClSi}$	$\text{Si}(\text{B}4)(\text{CH}_3)_3$	(bromochloromethyl)trimethylsilane [corrosive, flammable, flash point = 41 °C]		
$\text{C}_4\text{H}_{10}\text{Br}_2\text{Si}$	$\text{Si}(\text{B}2)_2(\text{CH}_3)_2$	bis(bromomethyl)dimethylsilane		106916-82-9
$\text{C}_4\text{H}_{10}\text{Br}_2\text{Si}$	$\text{Si}(\text{B}11)(\text{CH}_3)_3$	(dibromomethyl)trimethylsilane [BP = 49.5-51.5 °C]	73	2612-42-2
$\text{C}_4\text{H}_{11}\text{BrOSi}$	$\text{Si}(\text{B}5)(\text{CH}_3)_2\text{OH}$	(2-bromoethyl)dimethylsilanol		
$\text{C}_4\text{H}_{11}\text{BrSi}$	$\text{Si}(\text{B}2)(\text{CH}_3)_3$	(bromomethyl)trimethylsilane [corrosive, flammable, BP = 115.5 °C, flash point = 16 °C]	74	18243-41-9
$\text{C}_5\text{H}_7\text{BrCl}_2\text{Si}$	$(\text{B}16)=\text{SiCl}_2$	1,1-dichloro-4-bromo-1-sila-2-cyclohexene [BP at 1.5 Torr = 64-68 °C]	75	

TABLE 16. SELECTED SILANES WITH ORGANOCHLORINE GROUPS (continued).

Empirical formula	Structural formula	Name	Ref	CAS No.
$C_5H_9BrSi$	$Si(B12)(CH_3)_3$	(bromoethynyl)trimethylsilane [BP = 50 °C]	76	
$C_5H_{11}BrSi$	$Si(B13)(CH_3)_3$	(1-bromovinyl)trimethylsilane [BP (120 Torr) = 72-75 °C]	77	13683-41-5
$C_5H_{11}BrSi$	$Si(B6)(CH_3)_3$	( <i>trans</i> -2-bromovinyl)trimethylsilane [corrosive, flammable, BP = 50 °C]	78	41309-43-7
$C_5H_{12}Br_2Si$	$Si(B3)(CH_3)_3$	1,2-dibromoethyl)trimethylsilane [MP = -9 to -11 °C, BP at 8 Torr = 74-75 °C]	79	18146-08-2
$C_5H_{13}BrSi$	$Si(B5)(CH_3)_3$	(2-bromoethyl)trimethylsilane [Bp at 39 Torr = 64-65 °C]	79	18156-67-7
$C_6H_{11}BrSi$	$Si(B7)(CH_3)_3$	(3-bromo-1-propynyl)trimethylsilane [irritant, BP at 2 Torr = 44 °C]	80	38002-45-8
$C_6H_{13}BrSi$	$Si(B8)(CH_3)_3$	(2-bromoallyl)trimethylsilane [corrosive, flammable, BP = 82 °C]		
$C_6H_{14}Br_2Si$	$Si(B5)_2(CH_3)_2$	bis(2-bromoethyl)dimethylsilane		
$C_6H_{15}BrSi$	$Si(B14)(CH_3)$	(2-bromopropyl)trimethylsilane [BP at 6 Torr = 31 °C]	81	
$C_6H_{17}BrSi_2$	$Si(B2)(CH_3)_2Si(CH_3)_3$	(bromomethyl)pentamethyldisilane		
$C_7H_{15}BrOSi$	$Si(B9)(CH_3)_3$	[(2-bromo-1-butenyl)oxy]trimethylsilane		
$C_7H_{15}Br_3Si$	$Si(B10)(C_2H_5)_3$	triethyl(tribromomethyl)silane	82,83	

TABLE 16. SELECTED SILANES WITH ORGANOCHLORINE GROUPS (continued).

Empirical formula	Structural formula	Name	Ref	CAS No.
C <sub>7</sub> H <sub>16</sub> BrFSi	Si(B32)(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	triethyl(bromofluoromethyl)silane	84	
C <sub>7</sub> H <sub>18</sub> Br <sub>2</sub> Si <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> Si-(B15)-Si(CH <sub>3</sub> ) <sub>3</sub>	dibromobis(trimethylsilyl)methane [MP = 70 °C, BP at 10 Torr = 105 °C]	85	29955-10-0
C <sub>8</sub> H <sub>12</sub> BrNSi	Si(B17)(CH <sub>3</sub> ) <sub>3</sub>	2-bromo-6-(trimethylsilyl)pyridine [BP at 18 Torr = 114 °C]	86	59409-80-2
C <sub>8</sub> H <sub>15</sub> BrSi	Si(B12)(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	(bromoethynyl)triethylsilane [BP at 1.5 Torr = 50 °C]	76	38177-63-8
C <sub>8</sub> H <sub>17</sub> BrOSi	Si(B18)(CH <sub>3</sub> ) <sub>3</sub>	3-bromo-3-methyl-2-(trimethylsilyloxy)-1-butene [BP at 9 Torr = 63 °C]	87	69278-36-0
C <sub>9</sub> H <sub>13</sub> BrOSi	Si(B19)(CH <sub>3</sub> ) <sub>3</sub>	(3-bromophenoxy)trimethylsilane [BP at 6 Torr = 94 °C]	88	36971-28-5
C <sub>9</sub> H <sub>13</sub> BrOSi	Si(B20)(CH <sub>3</sub> ) <sub>3</sub>	(4-bromophenoxy)trimethylsilane [BP at 20 Torr = 122 °C]	89	17878-44-3
C <sub>9</sub> H <sub>13</sub> BrSi	Si(B21)(CH <sub>3</sub> ) <sub>3</sub>	(2-bromophenyl)trimethylsilane [BP at 18 Torr = 120 °C]	90	17878-37-4
C <sub>9</sub> H <sub>13</sub> BrSi	Si(B22)(CH <sub>3</sub> ) <sub>3</sub>	(3-bromophenyl)trimethylsilane [BP at 5 Torr = 94-96 °C]	88	17878-47-6
C <sub>9</sub> H <sub>13</sub> BrSi	Si(B23)(CH <sub>3</sub> ) <sub>3</sub>	(4-bromophenyl)trimethylsilane [BP at 32 Torr = 120.5-121 °C]	91	6999-03-7
C <sub>10</sub> H <sub>15</sub> BrSi	Si(B24)(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	(4-bromo-1,3-butadienyl)triethylsilane [Not obtained pure]	92	55552-44-8



TABLE 16. SELECTED SILANES WITH ORGANOCHLORINE GROUPS (concluded).

Empirical formula	Structural formula	Name	Ref	CAS No.
$C_{10}H_{15}BrSi$	$Si(B25)(CH_3)_3$	[(2-bromophenyl)methyl]trimethylsilane [BP at 3.5 Torr = 80-81 °C]	93	
$C_{10}H_{15}BrSi$	$Si(B26)(CH_3)_3$	[(3-bromophenyl)methyl]trimethylsilane [BP at 21 Torr = 132 °C]	93	1833-43-8
$C_{10}H_{15}BrSi$	$Si(B27)(CH_3)_3$	[(4-bromophenyl)methyl]trimethylsilane [BP at 3 Torr = 88-89 °C]	94	17095-20-4
$C_{10}H_{19}BrSi$	$Si(B28)(CH_3)_3$	7-bromo-7-(trimethylsilyl)bicyclo[4.1.0]heptane	95	43131-20-0
$C_{10}H_{29}BrSi_4$	$(B2)(CH_3)_2Si(CH_3)_2Si(CH_3)_2Si(CH_3)_2Si(CH_3)_3$	1-(bromomethyl)-1,1,2,2,3,3,4,4,4-nonamethyltetrasilane		62978-02-3
$C_{11}H_{16}Br_2OSi$	$Si(B29)(CH_3)_3$	[dibromo(4-methoxyphenyl)methyl]-trimethylsilane	96	76943-81-2
$C_{13}H_{21}BrSi_4$	$(B1)SiH_2SiH_2SiH_2SiH_2CH_2CH_2CH_2CH_3$	1-(4-bromo-1-naphthalenyl)-4-propyltetrasilane		102246-26-4
$C_{16}H_{19}BrSi$	$Si(B30)(CH_2CH_3)_3$	[4-(3-bromophenyl)-1,3-butadiyne]triethylsilane [BP at 0.8 Torr = 185 °C]	76	32117-60-50
$C_{19}H_{17}BrSi$	$Si(B13)(C_6H_5)_3$	(1-bromovinyl)triphenylsilane [MP = 132-134 °C]	97	18676-45-4
$C_{21}H_{19}BrSi$	$Si(B31)(C_6H_5)_3$	(2-bromo-1-methylethenyl)triphenylsilane [MP = 174-175 °C]	98	61979-41-7

TABLE 17. SELECTED SILANES WITH ORGANOFLUORINE GROUPS.

Empirical formula	Structural formula	Name	Ref	CAS No.
$\text{CH}_3\text{F}_3\text{Si}$	$\text{Si}(\text{A}3)\text{H}_3$	(trifluoromethyl)difluoroiodosilane	52	
$\text{CF}_3\text{SiI}$	$\text{Si}(\text{A}3)\text{F}_2\text{I}$	(trifluoromethyl)difluoroiodosilane	51	
$\text{CF}_6\text{Si}$	$\text{Si}(\text{A}3)\text{F}_3$	(trifluoromethyl)trifluorosilane	51	
$\text{C}_2\text{H}_4\text{F}_4\text{Si}$	$\text{Si}(\text{A}1)\text{H}_3$	(1,1,2,2-tetrafluoroethyl)silane		
$\text{C}_2\text{H}_3\text{F}_3\text{Si}$	$\text{Si}(\text{A}2)\text{H}_3$	(2,2,2-trifluoroethyl)silane		
$\text{C}_2\text{HF}_7\text{Si}$	$\text{Si}(\text{A}1)\text{F}_3$	trifluoro(1,1,2,2-tetrafluoroethyl)silane [BP = -4.5 °C]	99	4168-07-4
$\text{C}_2\text{H}_4\text{Cl}_3\text{F}_6\text{NSi}$	$\text{Si}(\text{A}9)\text{Cl}_3$	2-(trichlorosilyl)-N,N-bis(trifluoromethyl)-ethylamine [liquid, BP = 134 °C]	100	28871-58-1
$\text{C}_4\text{H}_4\text{F}_8\text{Si}$	$\text{Si}(\text{A}10)_4$	tetrakis(difluoromethyl)silane	101	
$\text{C}_4\text{H}_6\text{Cl}_2\text{F}_2\text{Si}$	$\text{Si}(\text{A}11)(\text{CH}_3)\text{Cl}_2$	1-(dichloro(2,2-difluorocyclopropyl)-methyl)silane [liquid, BP = 127-128 °C]	102	
$\text{C}_4\text{H}_7\text{Cl}_2\text{F}_3\text{Si}$	$\text{Si}(\text{A}12)(\text{CH}_3)\text{Cl}_2$	dichloromethyl(3,3,3-trifluoropropyl)silane [liquid, BP = 125 °C]	103	675-62-7
$\text{C}_4\text{H}_9\text{F}_3\text{Si}$	$\text{Si}(\text{A}3)(\text{CH}_3)_3$	trimethyl(trifluoromethyl)silane [flammable, irritant, BP = 140 °C]		
$\text{C}_4\text{H}_{10}\text{ClFSi}$	$\text{Si}(\text{A}4)(\text{CH}_3)_3$	(chlorofluoromethyl)trimethylsilane	104	
$\text{C}_4\text{H}_{11}\text{FSi}$	$\text{Si}(\text{A}5)(\text{CH}_3)_3$	(fluoromethyl)trimethylsilane [liquid, BP at 752 Torr = 64 °C]	105	28871-61-6

TABLE 17. SELECTED SILANES WITH ORGANOFLUORINE GROUPS (continued).

Empirical formula	Structural formula	Name	Ref	CAS No.
C <sub>5</sub> H <sub>9</sub> F <sub>3</sub> O <sub>2</sub> Si	Si(A13)(CH <sub>3</sub> ) <sub>3</sub>	trimethylsilyl trifluoroacetate [liquid, BP = 90.2 °C]	106	400-53-3
C <sub>6</sub> F <sub>8</sub> Si	Si(A7)F <sub>3</sub>	trifluoro(pentafluorophenyl)silane [liquid, thermally stable to at least 300 °C, readily hydrolyzed to polymeric materials, BP = 125 °C]	107	5272-26-4
C <sub>6</sub> H <sub>11</sub> F <sub>5</sub> OSi	Si(A6)(CH <sub>3</sub> ) <sub>3</sub>	trimethyl(3,3,3,2,2-pentafluoropropoxy)silane [BP = 93 °C]		
C <sub>7</sub> H <sub>15</sub> F <sub>3</sub> Si	Si(A3)(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	triethyl(trifluoromethyl)silane [MP = -156 °C, BP = 60 °C]		
C <sub>7</sub> H <sub>17</sub> FSi	Si(A5)(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	triethyl(fluoromethyl)silane	84	
C <sub>8</sub> H <sub>6</sub> ClF <sub>5</sub> Si	Si(A7)CH <sub>3</sub> ) <sub>2</sub> Cl	chlorodimethyl(pentafluorophenyl)silane [flammable, corrosive, BP at 10 Torr = 89 °C]		
C <sub>8</sub> H <sub>10</sub> F <sub>12</sub> O <sub>2</sub> Si	Si(A8) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>	dimethylbis[2-(trifluoromethyl)-3,3,3-trifluoroethoxy]silane		
C <sub>8</sub> H <sub>10</sub> F <sub>10</sub> O <sub>2</sub> Si	Si(A6) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>	dimethylbis[3,3,4,4,4-pentafluoropropoxy]silane		
C <sub>8</sub> H <sub>18</sub> F <sub>3</sub> NOSi <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> Si-(A14)-Si(CH <sub>3</sub> ) <sub>3</sub>	2,2,2-trifluoro-N,N-bis(trimethylsilyl)acetamide [BP = 47 °C]	108	21149-38-2
C <sub>8</sub> H <sub>18</sub> F <sub>3</sub> NOSi <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> Si-(A15)-Si(CH <sub>3</sub> ) <sub>3</sub>	trimethylsilyl ester of 2,2,2-trifluoro-N-(trimethylsilyl)ethanimidic acid [MP = -41 °C, BP = 142 °C]	109	25561-30-2

TABLE 17. SELECTED SILANES WITH ORGANOFLUORINE GROUPS (concluded).

Empirical formula	Structural formula	Name	Ref	CAS No.
C <sub>9</sub> H <sub>13</sub> FSi	Si(A16)(CH <sub>3</sub> ) <sub>3</sub>	(2-fluorophenyl)trimethylsilane [liquid, BP = 167-168 °C]	110	1842-26-8
C <sub>9</sub> H <sub>13</sub> FSi	Si(A17)(CH <sub>3</sub> ) <sub>3</sub>	(3-fluorophenyl)trimethylsilane [BP at 60 Torr = 70-74 °C]	110	7217-41-6
C <sub>9</sub> H <sub>13</sub> FSi	Si(A18)(CH <sub>3</sub> ) <sub>3</sub>	(4-fluorophenyl)trimethylsilane [BP at 17 Torr = 56 °C]	110	455-17-4
C <sub>9</sub> H <sub>14</sub> FNSi	Si(A19)(CH <sub>3</sub> ) <sub>3</sub>	(4-fluorophenylamino)trimethylsilane [liquid, BP at 21 Torr = 106-107 °C]	111	33407-00-0
C <sub>10</sub> H <sub>9</sub> F <sub>18</sub> O <sub>3</sub> Si	Si(A6) <sub>3</sub> (CH <sub>3</sub> )	methyltris[3,3,4,4,4-pentafluoropropoxy]silane		
C <sub>11</sub> H <sub>13</sub> F <sub>5</sub> Si	Si(A20)(CH <sub>3</sub> ) <sub>3</sub>	trimethyl[2-pentafluorophenyl]ethyl]silane [BP at 6 Torr = 88-89 °C]	112	35943-75-0
C <sub>18</sub> HF <sub>15</sub> Si	Si(A7) <sub>3</sub> H	tris(pentafluorophenyl)silane [solid, MP = 133 °C]	113	20160-40-1
C <sub>18</sub> H <sub>13</sub> F <sub>3</sub> Si	Si(A17) <sub>3</sub> H	tris(3-fluorophenyl)silane [BP at 0.8 Torr = 148-151 °C]	114	20240-78-2
C <sub>18</sub> H <sub>13</sub> F <sub>3</sub> Si	Si(A18) <sub>3</sub> H	tris(4-fluorophenyl)silane	114	1691-36-7
C <sub>21</sub> H <sub>13</sub> F <sub>9</sub> Si	Si(A21) <sub>3</sub> H	tris[3-(trifluoromethyl)phenyl]silane [BP at 0.05 Torr = 147-150 °C]	115	386-92-5
C <sub>21</sub> H <sub>13</sub> F <sub>9</sub> Si	Si(A22) <sub>3</sub> H	tris[4-(trifluoromethyl)phenyl]silane [solid, MP = 82-83 °C]	116	386-96-9

## K. PROPOSED SILANES AND SYNTHETIC ROUTES

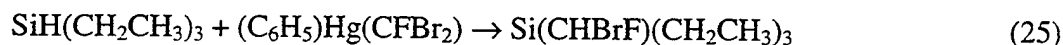
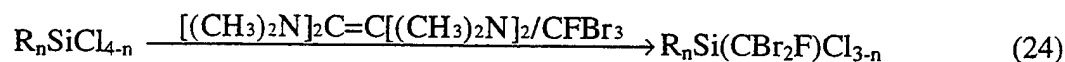
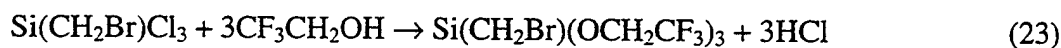
The silanes that appear to be most promising as halon replacements are compounds of the type  $\text{Si}(\text{R}')(\text{R}'')_3$ , where  $\text{R}'$  is a bromoalkyl compound from the group of substituents  $-\text{CH}_2\text{Br}$  (B2),  $-\text{CHBrCl}$  (B4),  $-\text{CHBr}_2$  (B11),  $-\text{CHBrF}$  (B32), and  $-\text{CBr}_2\text{F}$  (B33) and  $\text{R}''$  is any other alkyl or alkoxy group.

It would be preferable to have  $\text{R}''$  highly fluorinated; however, as pointed out earlier, groups containing fluorine in the alpha position to silicon tend to be unstable. Should stability not be a problem,  $-\text{CF}_3$  derivatives can be prepared. The low-temperature reaction of  $\text{SiF}_2$  with  $\text{CF}_3\text{I}$  gives  $\text{Si}(\text{CF}_3)_2\text{F}_2$ , which can then be converted to other products (Reference 28). The three-component reaction of tris(diethylamino)phosphine,  $[(\text{CH}_3\text{CH}_2)_3\text{N}]_3\text{P}$ ; bromotrifluoromethane,  $\text{CF}_3\text{Br}$ ; and alkylchlorosilanes, has allowed the preparation of the compounds  $\text{SiR}_3(\text{CF}_3)$ ,  $\text{SiR}_2(\text{CF}_3)\text{Cl}$ ,  $\text{SiR}_2(\text{CF}_3)_2$ ,  $\text{SiR}(\text{CF}_3)_2\text{Cl}$ , and  $\text{SiR}(\text{CF}_3)\text{Cl}_2$  (Reference 117). The reaction apparently proceeds through the formation of the intermediate  $[(\text{CH}_3\text{CH}_2)_3\text{N}]_3\text{PBr}^+ \text{CF}_3^-$ . Another excellent trifluoromethylating agent is formed by reaction of tetrakis(dimethylamino)ethylene  $((\text{CH}_3)_2\text{NC}=\text{CN}(\text{CH}_3)_2)$  and trifluoromethyl iodide ( $\text{CF}_3\text{I}$ ) to give charge-transfer complex (Reference 118). Reaction with compounds of the type  $\text{R}_3\text{SiCl}$  allows replacement of the chlorine by a  $-\text{CF}_3$  group. If bromine can be present in the  $\text{R}_3\text{SiCl}$  starting material, it may be possible to use this method to prepare compounds of the type  $\text{R}_3\text{SiCF}_3$ , where one or more of the R substituents contain bromine.

If  $-\text{CF}_3$  groups are to be avoided,  $\text{R}'' = -\text{CH}_2\text{CF}_3$  (A2),  $-\text{OCH}_2\text{CF}_3$  (A23),  $-\text{OCH}_2\text{CF}_2\text{CF}_3$  (A6),  $-\text{OCH}_2(\text{CF}_3)_2$  (A8), and, possibly,  $-\text{CH}_2\text{CH}_2\text{CF}_3$  (A12) appear to be the substituents of choice. The alkoxy derivatives are expected to be the most easily prepared and are likely to have even shorter atmospheric lifetimes owing to the presence of hydrogen atoms in the alpha position relative to the oxygen (Reference 33). For these reasons the substituents A2 and A12 are not considered further at this point. Of course, depending on the results of fire suppression, toxicity, and other testing, these substituents could be reconsidered. It should be noted that alkoxy

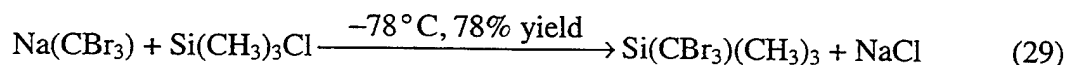
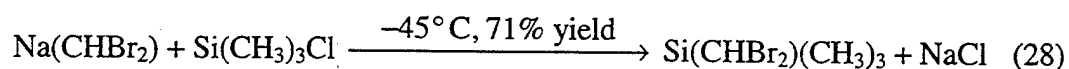
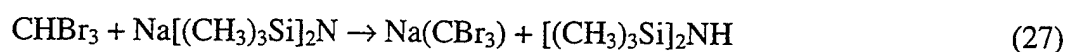
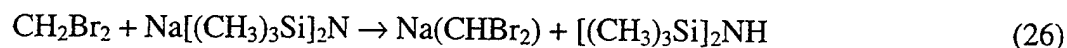
derivatives may have a toxicity problem. There is some evidence that some can cause blindness, and this needs to be investigated further.

$\text{Si}(\text{CH}_2\text{Br})\text{Cl}_3$  has been prepared (Reference 69), and this could be reacted with a number of fluorinated alcohols, the most promising of which would be  $\text{CF}_3\text{CH}_2\text{OH}$ , thus allowing the formation of  $\text{Si}(\text{CH}_2\text{Br})(\text{OCH}_2\text{CF}_3)_3$  (Reaction 23). A similar synthetic route could be used for the formation of  $\text{Si}(\text{CHBrF})(\text{OCH}_2\text{CF}_3)_3$  and  $\text{Si}(\text{CBr}_2\text{F})(\text{OCH}_2\text{CF}_3)_3$ . Substituted derivatives of one of the starting materials,  $\text{R}_n\text{Si}(\text{CBr}_2\text{F})\text{Cl}_{3-n}$ , have been prepared by reaction of tribromofluoromethane with  $\text{R}_n\text{SiCl}_{4-n}$  (Reaction 24; Reference 119). The derivatives include products where R is methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, and *s*-butyl. Other proposed alcohols are  $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$  and  $(\text{CF}_3)_2\text{CH}_2\text{OH}$  to give the corresponding  $-\text{OCH}_2\text{CF}_2\text{CF}_3$  and  $-\text{OCH}_2(\text{CF}_3)_2$  derivatives. In addition  $\text{Si}(\text{CBr}_2\text{F})(\text{CH}_3)_3$  and  $\text{Si}(\text{CHBrF})(\text{CH}_3)_3$  should be tested, although it is possible that these are flammable. Synthesis of the first compound has been reported (Reference 119), and the ethyl derivative, rather than the methyl derivative of the second compound, has been prepared by insertion of  $\text{CFBr}$  into the  $\text{SiH}$  bond of triethylsilane (Reference 84). This reaction (Reaction 25) involves generation of the carbene  $:\text{CFBr}$  from phenyl(fluorodibromomethyl)mercury ( $(\text{C}_6\text{H}_5)\text{Hg}(\text{CFBr}_2)$ ), which can be prepared from phenylmercuric chloride ( $(\text{C}_6\text{H}_5)\text{HgCl}$ ) and dibromofluoromethane ( $\text{CHFBr}_2$ ), in the presence of a strong base such as potassium *t*-butoxide ( $(\text{CH}_3)_3\text{COK}$ ).  $\text{Si}(\text{CH}_2\text{Br})_2(\text{CH}_3)_2$  has been prepared, and this compound is of particular interest in view of its large bromine content. It may be that additional fluorination is not needed.



$\text{Si}(\text{CHBr}_2)(\text{CH}_3)_3$  and  $\text{Si}(\text{CBr}_3)(\text{CH}_3)_3$  have large bromine contents, and synthetic procedures are available (Reference 73). These materials are prepared by reacting the sodium salts  $\text{NaCHBr}_2$  or  $\text{NaCBr}_3$  (formed from reaction of sodium bis(trimethylsilyl)amide,  $\text{Na}[(\text{CH}_3)_3\text{Si}]_2\text{N}$ , in a solution of anhydrous ether with the appropriate halocarbon, Reaction 26 or

27) with trimethylchlorosilane,  $\text{Si}(\text{CH}_3)_3\text{Cl}$  (Reaction 28 or 25). The preparation was carried out by introducing 0.1 mole of  $\text{Na}[(\text{CH}_3)_3\text{Si}]_2\text{N}$  into 50 mL of a solution prepared by mixing 0.11 mole of the halocarbon ( $\text{CH}_2\text{Br}_2$  or  $\text{CHBr}_3$ ), 0.15 mole of  $\text{Si}(\text{CH}_3)_3\text{Cl}$ , and 200 mL of anhydrous ether.  $\text{Si}(\text{CHBrCl})(\text{CH}_3)_3$  and  $(\text{CH}_3)_3\text{SiCBr}_2\text{Si}(\text{CH}_3)_3$  can be prepared in a similar manner. In theory, one should be able to carry out these reactions with fluorinated alkyl groups in place of one or more of the methyl groups in  $\text{Si}(\text{CH}_3)_3\text{Cl}$ .



The compound  $\text{Si}(\text{CH}_3)_3(\text{CF}_2\text{Br})$  (boiling point, 105 to 106 °C) has been prepared in a 10-percent yield from reaction of  $[(\text{CH}_3\text{CH}_2)_3\text{N}]_3\text{P}$  with bromotrimethylsilane,  $\text{Si}(\text{CH}_3)_3\text{Br}$  and bromochlorodifluoromethane,  $\text{CBrClF}_2$  (Reference 104).

Based on the information in this section, the silanes listed in Table 18 are proposed for testing as halon substitutes.

TABLE 18. SILANES RECOMMENDED FOR PREPARATION AND TESTING.

Substituents	Compound
Methyl derivatives	
B11	$\text{Si}(\text{CHBr}_2)(\text{CH}_3)_3$
B10	$\text{Si}(\text{CBr}_3)(\text{CH}_3)_3$
B2	$\text{Si}(\text{CH}_2\text{Br})_2(\text{CH}_3)_2$
B33	$\text{Si}(\text{CBr}_2\text{F})(\text{CH}_3)_3$
B32	$\text{Si}(\text{CHBrF})(\text{CH}_3)_3$
2,2,2-Trifluoroethoxy derivatives	
B11, A23	$\text{Si}(\text{CHBr}_2)(\text{OCH}_2\text{CF}_3)_3$
B10, A23	$\text{Si}(\text{CBr}_3)(\text{OCH}_2\text{CF}_3)_3$
B2, A23	$\text{Si}(\text{CH}_2\text{Br})_2(\text{OCH}_2\text{CF}_3)_2$
B33, A23	$\text{Si}(\text{CBr}_2\text{F})(\text{OCH}_2\text{CF}_3)_3$
B32, A23	$\text{Si}(\text{CHBrF})(\text{OCH}_2\text{CF}_3)_3$
3,3,3,2,2-Pentafluoropropoxy	
B11, A6	$\text{Si}(\text{CHBr}_2)(\text{OCH}_2\text{CF}_2\text{CF}_3)_3$
B10, A6	$\text{Si}(\text{CBr}_3)(\text{OCH}_2\text{CF}_2\text{CF}_3)_3$
B2, A6	$\text{Si}(\text{CH}_2\text{Br})_2(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$
B33, A6	$\text{Si}(\text{CBr}_2\text{F})(\text{OCH}_2\text{CF}_2\text{CF}_3)_3$
B32, A6	$\text{Si}(\text{CHBrF})(\text{OCH}_2\text{CF}_2\text{CF}_3)_3$



## SECTION VII

### SILOXANES

Siloxanes ("silicones") are either linear or cyclic and have the general structures shown in Figure 9, where "n" or "x" is an integer giving the number of repeating units. As in silicate minerals, the siloxane group, Si-O-Si confers thermal stability on organosiloxanes, but to a greater or lesser extent since the stability is lowered by the presence of organic groups. The siloxane bond is susceptible to attack by a variety of reagents. High-pressure steam splits the bond to give two silanol groups. In this way, high molecular weight polysiloxanes can be converted to lower molecular weight polysiloxanes.

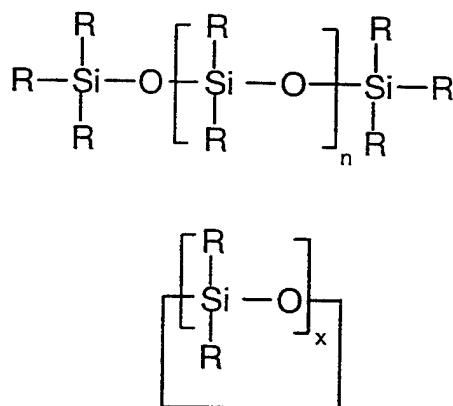


Figure 9. Siloxane Structures.

#### A. ALKYL SILOXANES

Methyl is the most common alkyl substituent in commercial siloxanes (i.e., R is CH<sub>3</sub> in Figure 9). For the two functional groups most commonly found ((CH<sub>3</sub>)<sub>2</sub>SiO, the repeating unit in linear and cyclic polysiloxanes, and CH<sub>3</sub>SiO<sub>1.5</sub>, the repeating unit in cross-linked polysiloxanes), only 40.5 percent and 22.4 percent, respectively, of carbon plus hydrogen are present. Although siloxanes are relatively thermally stable, the linear siloxanes do rearrange to cyclic siloxanes when heated in the absence of oxygen at temperatures around 400 °C (Reference 24).

Higher molecular weight polymethylsiloxanes and polyethylsiloxanes have been commercially available for use in lubrication and hydraulics for many years (Reference 120). The materials have remarkably low temperature coefficients of viscosity and an unusual resistance to thermal oxidation in air. The flash points are much higher than those of hydrocarbons of the same viscosity; however, the flash points of the polyethylsiloxanes are lower than the polymethylsiloxanes by about 37.7 °C (100 °F) or more. This is not unexpected since the polyethyl derivatives are more hydrocarbon-like. The flammability properties of polymethylsiloxanes and poly(methylphenyl)siloxanes having viscosities at 37.7 °C (100 °F) of 20 cSt or more, when stripped of volatile components, have been summarized (Reference 120): "The flash points are high; when the liquids are ignited the flames are readily extinguished; the spontaneous ignition temperatures are high; the spray flammability limits are high; and they are practically nonflammable to incendiary fire."

Lower molecular weight methylsiloxanes (called volatile methylsiloxanes [VMS]) are now being considered as cleaning agents and are being commercialized by Dow Corning Corporation (Reference 121). The commercialized compounds have the general structure  $(\text{CH}_3)_3\text{Si}-[\text{OSi}(\text{CH}_3)_2]_n-\text{Si}(\text{CH}_3)_3$ , where  $n$  varies from 0 to 3. VMSs are of high purity and relatively easy to recover and recycle. Of particular importance is that the atmospheric lifetimes of these or similar compounds are between 10 and 30 days (Reference 122), and they have a zero ozone depletion potential (ODP). Though, the materials exhibit flash points at relatively low temperatures, halogen substitution should eliminate flammability. Properties of some of the commercialized VMS materials are shown in Table 19.

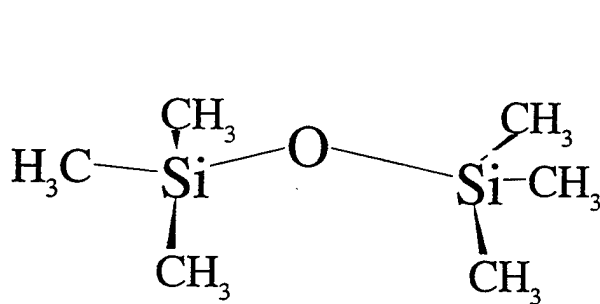
TABLE 19. VOLATILE METHYLSILOXANES MARKETING BY DOW CORNING CORPORATION.

	OS-10	OS-20	OS-30	OS-90
Compound	Hexamethyl- disiloxane	Octamethyl- trisiloxane	Decamethyl- tetrasiloxane	
Flash Point, closed cup, °C (°F)	-1 (30)	34 (94)	57 (135)	74 (165)
Boiling Point at 760 Torr, °C (°F)	100 (212)	149 (300)	192 (378)	217 (423)
Evaporation Rate ( <i>n</i> -Butyl Acetate = 1.0)	3	1	0.1	0.04
Viscosity at 25 °C (77 °F), cSt	0.65	1.0	1.5	5.0
Specific Gravity at 25 °C (77°F)	0.761	0.82	0.85	0.96
Surface Tension at 25 °C (77°F), dynes/cm	15.9	16 <sup>a</sup>	18	21
Freezing Point, °C (°F)	-68 (-90)	-82 (-115) <sup>a</sup>	-76 (-105)	-44 (-47)
Heat of Vaporization at 65 °C (150 °F), joule/g <sup>a</sup>	192	184	151	105

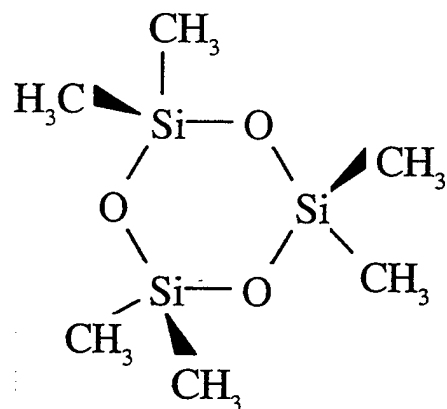
<sup>a</sup> Estimated.

The vapor pressures of several methylsiloxanes (Figure 10) have been reported (Reference 123). For hexamethyldisiloxane ((CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub>), hexamethylcyclotrisiloxane ([ (CH<sub>3</sub>)<sub>2</sub>SiO ]<sub>3</sub>), octamethylcyclotetrasiloxane, ((CH<sub>3</sub>)<sub>2</sub>SiO)<sub>4</sub>, and decamethylcyclopentasiloxane ([ (CH<sub>3</sub>)<sub>2</sub>SiO ]<sub>5</sub>), the vapor pressures at 297 k are 40, 8.0, 0.97, and 0.17 Torr. These data indicate that methylsiloxanes should contain no more than three silicon atoms to provide vapor pressures suitable for use in preparing halon replacements for total-flood applications. On the other hand, for streaming, smaller vapor pressures may be suitable. Furthermore, substitution by fluorine is likely to increase the vapor pressure. Octamethylcyclotetrasiloxane has a melting point of 17 °C and a boiling point of 175 °C. What is particularly interesting is that octamethyltrisiloxane (Figure 11), which has a lower molecular weight than the cyclic compound, is a solid. This indicates that closed ring compounds may be more volatile and, therefore, more desirable as

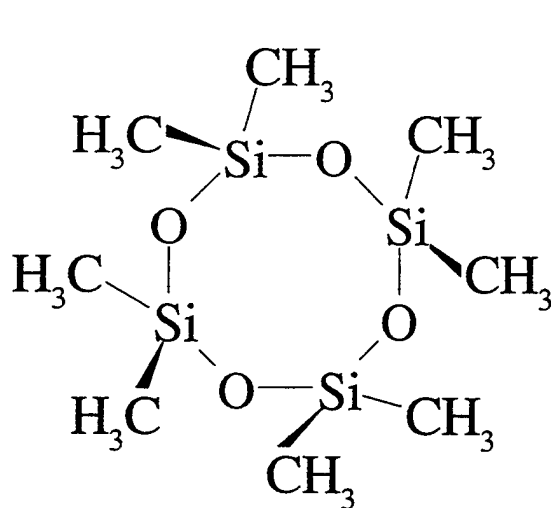
parent molecules. Derivatives of cyclodisiloxane (Figure 12) may be particularly applicable; however, these compounds are stable only with bulky organic substituents.



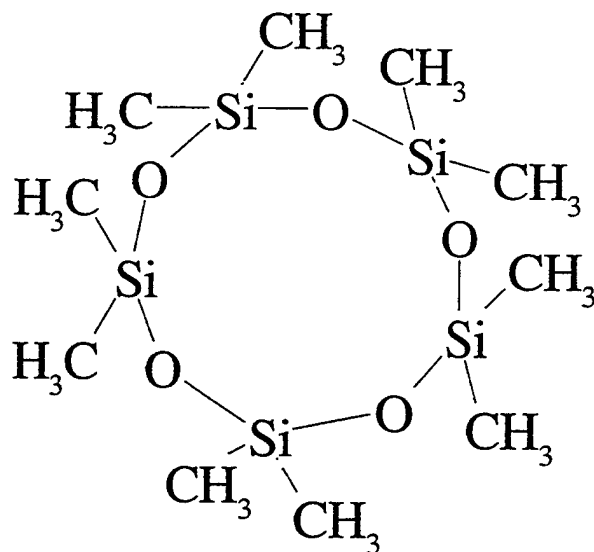
Hexamethyldisiloxane



Hexamethylcyclotrisiloxane



Octamethylcyclotetrasiloxane



Decamethylcyclopentasiloxane

Figure 10. Methylsiloxanes.

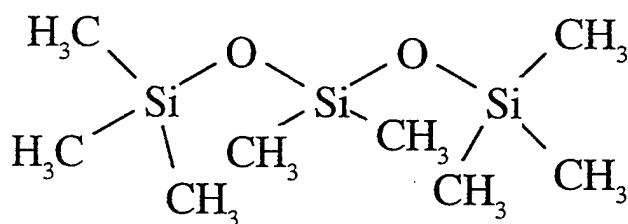


Figure 11. Octamethyltrisiloxane.

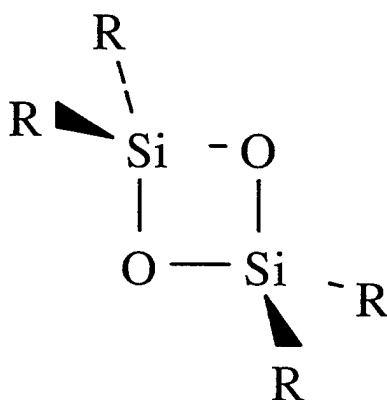


Figure 12. Tetramethylcyclodisiloxane

## B. PREPARATION

The most important method for making siloxanes is the hydrolysis of chlorosilanes followed by condensation of the resulting silanols. Hydrolytic cleavage of Si-Cl gives Si-OH (Reaction 30). In most cases, the Si-OH group undergoes condensation, forming siloxanes (Reaction 31). Two hydroxyl groups attached to the same silicon atom spontaneously eliminate water but do not give silicon doubly linked to oxygen. In this case, a condensed material is always formed. Hydrolysis of trichlorophenylsilane gives brittle resins that are fusible and soluble in organic solvents due to incomplete condensation. Long heating gives complete

condensation to an infusible and more insoluble material. The introduction of chlorine into the aromatic nuclei makes the product more resistant to oxidation and less flammable. Substitution by other halogens produces similar effects (References 124 and 125).



Although the direct reaction of silicon halides with water is the most common method for the production of siloxanes, several alternatives exist. These alternatives are useful when well-defined substituents on each silicon atom are desired. For example, organosilanes can be converted to silanols, siloxanes, or mixtures of these by reaction with sodium bicarbonate or bisulfite under substantially anhydrous conditions.

In forming siloxanes, silicon can have a functionality of one, two, three, or four, giving a variety of molecular types. The methyl siloxanes represent the series that has been most intensively studied, and the various possibilities are illustrated from a consideration of this series.

Monofunctional Compounds. The hydrolysis of chlorotrimethyl silane with water proceeds readily to give hexamethyl disiloxane. For ease in writing complicated structures the monofunctional unit  $(\text{CH}_3)_3\text{SiO-}$  may be written **M**.

Difunctional Compounds. Hydrolysis of dichlorodimethylsilane or diethoxydimethylsilane gives rise to difunctional units  $-\text{Si}(\text{CH}_3)_2\text{O-}$ , conveniently represented by **D**, and these can form both linear and cyclic structures. The linear structures will always have functional silanol end groups that can react further, but the cyclic compounds lack functionality.

Linear polymers that have low average molecular weight and hence low viscosity and that contain silanol end groups tend to increase spontaneously in molecular weight and viscosity on standing. More thermally stable linear polymers within a large range of molecular size can be made by combining monofunctional and difunctional units to give chain-stopped fluids of the general formula **M(D)<sub>n</sub>M**. The average molecular weight of the fluid is controlled mainly by the proportions of the monofunctional to difunctional units.

If one considers the increasing boiling points and the low melting points of the compounds and extrapolates the values for chains of still greater length, one finds that there is a series of methylpolysiloxanes of very wide liquid range. Since the compounds are "chain stoppered" and are incapable of further condensation, they are chemically stable and are unaffected by high temperatures or most chemical reagents. Such linear methylpolysiloxanes are the basis for silicone oils or silicone fluids designed to withstand extremes of temperature and to be inert to metals and most chemical reagents.

A generally satisfactory method of obtaining molecules of the desired size alone, and hence of desired viscosity and operating temperature range, involves a catalytic rearrangement of monofunctional and difunctional siloxane units. This method for preparing methylpolysiloxane liquids of predetermined molecular size permits the design of silicone oils from data obtained on pure molecular species.

The vapor pressures at several temperatures have been measured for the linear methylsiloxane polymers with chains of 2 to 11 silicon atoms and the heats of vaporization have been found to fit Equation 2 (Reference 126).

$$\Delta H_{\text{vap linear}} = 4.70 + 1.65x \text{ kcal} \quad [2]$$

where  $x$  is the number of silicon atoms in the chain. The same information gained from a study of the cyclic polymers of dimethylsiloxane, from the tetramer to the octamer, gives heats of vaporization that fit Equation 3.

$$\Delta H_{\text{vap cyclic}} = 5.45 + 1.35x \text{ kcal} \quad [3]$$

where  $x$  again is the number of silicon-containing units (Reference 126). At a given temperature, a cyclic polymer always has a higher vapor pressure than a linear polymer with the same number of silicon atoms. The cyclic polymers also always have a higher viscosity than the linear polymers of the same number of units. The cyclic forms also change their viscosities more rapidly with temperature. The remarkably small change in viscosity with temperature shown by

the linear methylpolysiloxanes sets them apart from hydrocarbon liquids and from other siloxane polymers.

Whereas the chemical properties of the methylpolysiloxanes derive from the nature of the siloxane bonds and the methyl-to-silicon links and do not change much with changes in polymer size, the freezing points depend on the molecular size and configuration. If a typical silicone oil is compared with a standard hydrocarbon oil, the two having the same viscosity at 37.7 °C (100 °F), we find that after cooling to -37.2 °C (-35 °F) the silicone oil has 7 times its original viscosity while the hydrocarbon oil has increased 1800 times in viscosity.

### ALKYLSILOXANES

It becomes progressively more difficult to make large polymers of alkylsiloxanes as the alkyl groups increase in size and the condensation of silanol groups becomes more sluggish. Ethyl, propyl, butyl, and amyl compounds of the type  $(R_2SiO)_x$  are all colorless, oily liquids. The corresponding  $(RSiO_{1.5})_x$  compounds are infusible solids. In general, the properties of the higher alkyl siloxanes are dominated less by the siloxane backbone, so that they are more oxidizable, show greater change in viscosity with change of temperature, and are more compatible with organic materials. Polysiloxanes containing benzyl and cyclohexyl groups resemble strongly those containing higher alkyl groups. The presence of unsaturated groups, such as vinyl and allyl attached to silicon in polysiloxanes, introduces the possibility of polymerization through their organic groups as well as copolymerization with unsaturated purely organic materials, but further increases the ease of oxidation (Reference 127).

The vapor pressures of the higher viscosity silicone oils depend markedly on the extent to which the more volatile fractions have been removed. This is also reflected in the flash point and spontaneous flammability temperatures of these oils. Properly stripped, silicones have flash points varying from below 25 °C to 350 °C for higher viscosity materials. The spontaneous flammability temperatures vary from 475 °C to 550 °C. In general, ethyl siloxanes are more flammable than methylsiloxanes, but replacing methyl groups with phenyl groups has little effect.



Silicone fluids are particularly notable for their heat stability and their resistance to oxidation. If oxygen is excluded they can be heated to temperatures around 400 °C before any appreciable thermal degradation occurs. At that temperature, the siloxane chain rearranges fairly rapidly and low boiling cyclic siloxanes are evolved, with the Si-C bonds remaining intact. At lower temperatures, this process is very much slower and can cause in time a slight decrease in viscosity of silicone oils. When oxygen (or air) is present the organic groups in particular are attacked; however, a certain minimum temperature has to be attained before oxidation becomes appreciable. This temperature has been determined for some substituent organic groups (Table 20) (Reference 24).

TABLE 20. OXIDATION TEMPERATURES OF SILICONES.

Substituent	Oxidative temperature, °C
butyl	120
ethyl	138
methyl	200

Thus, polymethylsiloxanes are stable to oxygen below 170 °C but are slowly attacked at temperatures of about 200 °C. The immediate and volatile products of oxidation are formaldehyde and water, while the silicone becomes cross-linked, leading eventually to gelation and finally the formation of silica. The polymethylphenylsiloxanes are somewhat more resistant than the polymethylsiloxanes to oxidation at high temperature.

Silicones are very poor solvents, the polymethylsiloxanes being the worst. In general, the latter will not dissolve a solid except at a temperature near its melting point and then only to a small extent and only if the solid is nonionic. It is, for example, very difficult to dye liquid silicones.

When dimethyldichlorosilane is hydrolyzed simply by stirring with a large excess of water, a colorless oil containing a large variety of molecular species is formed. About half of the oil consists of cyclic polymers of dimethylsiloxane of the type  $[(CH_3)_2SiO]_x$ , where x is an

integer greater than two. These may be distilled from the oil at temperatures up to 200 °C and pressures as low as 1 Torr (Reference 55).

If insufficient water for complete hydrolysis is supplied, and in a mutual solvent such as ether, there is formed a series of complex dichlorosilanes of the type  $\text{Cl}[\text{Si}(\text{CH}_3)_2\text{O}]_x\text{Si}(\text{CH}_3)_2\text{Cl}$ , where x is unity or a small integer.

#### D. HALOGENATED SILOXANES

Brominated siloxanes, usually denoted as silicon oxybromides, are prepared by heating silicon in an  $\text{O}_2/\text{Br}_2$  mixture at about 700 °C (Reference 128). They have the form  $\text{Br}_3\text{Si}-[\text{OSiBr}_2]_x-\text{O}-\text{SiBr}_3$  and are the homologs of the polymethylsiloxanes. The silicon oxybromides are also colorless fluids at room temperature. The oxybromides of silicon are very rapidly hydrolyzed in moist air and their thermal decomposition takes place easily at modest temperatures.

#### E. TABLES OF PHYSICAL PROPERTIES OF SILOXANES.

The physical properties of some of the linear dimethylsiloxanes are given in Table 21, properties of the cyclic dimethylsiloxanes are presented in Table 22, and properties of the linear dichlorodimethylsiloxanes are presented in Table 23 (References 126 and 129). Table 24 contains some additional properties for silicone fluids.

TABLE 21. LINEAR METHYLPOLYSILOXANES.

Compound	Empirical formula	Boiling point, °C		Melting point, °C
		760 Torr	20 Torr	
$\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_2\text{Si}(\text{CH}_3)_3$	$\text{C}_8\text{H}_{24}\text{O}_2\text{Si}_3$	153	---	≈-80
$\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_3\text{Si}(\text{CH}_3)_3$	$\text{C}_{10}\text{H}_{30}\text{O}_3\text{Si}_4$	194	---	≈-70
$\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_4\text{Si}(\text{CH}_3)_3$	$\text{C}_{12}\text{H}_{36}\text{O}_4\text{Si}_5$	229	---	≈-80
$\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_5\text{Si}(\text{CH}_3)_3$	$\text{C}_{14}\text{H}_{42}\text{O}_5\text{Si}_6$	---	142	<-100
$\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_6\text{Si}(\text{CH}_3)_3$	$\text{C}_{16}\text{H}_{48}\text{O}_6\text{Si}_7$	190	---	≈-80

TABLE 22. CYCLIC METHYLPOLYSILOXANES.

Compound	Empirical formula	Boiling point, °C		Melting point, °C
		760 Torr	20 Torr	
$[(CH_3)_2SiO]_3$	$C_6H_{18}O_3Si_3$	134	--	64
$[(CH_3)_2SiO]_4$	$C_8H_{24}O_4Si_4$	175	74	17.5
$[(CH_3)_2SiO]_5$	$C_{10}H_{30}O_5Si_5$	210	101	-38
$[(CH_3)_2SiO]_6$	$C_{12}H_{36}O_6Si_6$	245	128	-3
$[(CH_3)_2SiO]_7$	$C_{14}H_{42}O_7Si_7$	---	154	-26
$[(CH_3)_2SiO]_8$	$C_{16}H_{48}O_8Si_8$	---	175	$\approx 30$
$[(CH_3)_2SiO]_9$	$C_{18}H_{54}O_9Si_9$	---	$\approx 188$	---

TABLE 23. METHYLCHLOROPOLYSILOXANES.

Compound	Empirical formula	Boiling point, °C		Melting point, °C
		760 Torr	20 Torr	
$Cl[(CH_3)SiO]_1Si(CH_3)_2Cl$	$C_3H_9Cl_2OSi_2$	138	41	-37
$Cl[(CH_3)SiO]_2Si(CH_3)_2Cl$	$C_4H_{12}Cl_2O_2Si_3$	184	79	-53
$Cl[(CH_3)SiO]_3Si(CH_3)_2Cl$	$C_5H_{15}Cl_2O_3Si_4$	222	111	-62
$Cl[(CH_3)SiO]_4Si(CH_3)_2Cl$	$C_6H_{18}Cl_2O_4Si_5$	---	138	$\approx -80$
$Cl[(CH_3)SiO]_5Si(CH_3)_2Cl$	$C_7H_{21}Cl_2O_5Si_6$	---	161	$\approx -80$

TABLE 24. PHYSICAL PROPERTIES OF SILICONE FLUIDS.

Viscosity	Molecular weight	Number of $(\text{CH}_3)_2\text{SiO}$ units	Pour point, °C	Freezing point, °C
0.65	162	1	---	-68
2.0	384	4	---	-84
10	1200	15	-67	---
20	1900	24	-60	---
100	6700	89	-55	---
350	15800	213	-50	---
1000	26400	355	-50	---
2000	35000	472	---	-48
12500	63400	855	---	

When methylsiloxanes are crosslinked, a series of resins is formed. This crosslinking results in a R/Si ratio always less than 2 and can be attained by several methods that utilize dimethyldichlorosilane as the feedstock. The methyl silicone resins have many very interesting properties but are not promising as fire suppressants.

Table 25 gives some data on a number of siloxanes that have been synthesized in the laboratory or are commercially available along with some notes on their properties (References 45, 124, 125, 127, and 129-137).

TABLE 25. SILOXANES.

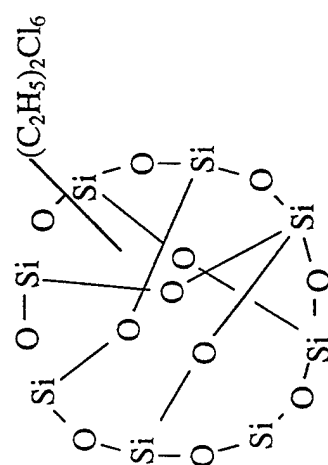
Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
Cl <sub>6</sub> OSi <sub>2</sub>	Cl <sub>3</sub> SiOSiCl <sub>3</sub>	hexachlorodisiloxane	28	137	C
H <sub>6</sub> OSi <sub>2</sub>	H <sub>3</sub> SiOSiH <sub>3</sub>	disiloxane	-144	-15	
CH <sub>3</sub> Cl <sub>3</sub> OSi <sub>2</sub>	Cl <sub>3</sub> SiOSiCl <sub>2</sub> (CH <sub>3</sub> )	pentachloromethyl-disiloxane			
C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub> OSi <sub>2</sub>	Cl <sub>3</sub> SiOSiCl <sub>2</sub> (CH=CH <sub>2</sub> )	pentachloroethenyl-disiloxane			
C <sub>2</sub> H <sub>3</sub> Cl <sub>7</sub> O <sub>2</sub> Si <sub>3</sub>	Cl <sub>3</sub> SiOSiCl <sub>2</sub> OSiCl <sub>2</sub> (CH=CH <sub>2</sub> )	1,1,1,3,3,5,5-heptachloro-5-ethenyl-trisiloxane			
C <sub>2</sub> H <sub>6</sub> F <sub>4</sub> OSi <sub>2</sub>	(CHF <sub>2</sub> )H <sub>2</sub> SiOSi(CHF <sub>2</sub> )H <sub>2</sub>	1,3-bis(difluoromethyl)-disiloxane			
C <sub>3</sub> H <sub>9</sub> Cl <sub>2</sub> OSi <sub>2</sub>	Cl[(CH <sub>3</sub> )SiO]Si(CH <sub>3</sub> ) <sub>2</sub> Cl	dichlorodimethyl-methylsiloxane			
C <sub>4</sub> H <sub>10</sub> Cl <sub>6</sub> O <sub>12</sub> Si <sub>8</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>6</sub> 	hexachlorodiethylpentacyclo-[9.5.1.1 <sup>3,9</sup> .1 <sup>5,15</sup> .1 <sup>7,13</sup> ]octasiloxane			
C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub> OSi <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> ClSiOSi(CH <sub>3</sub> ) <sub>2</sub> Cl	1,1-dichloro-1,1,3,3-tetramethyl-disiloxane			

TABLE 25. SILOXANES (continued).

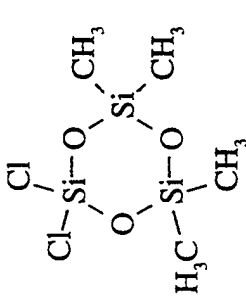
Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub> O <sub>3</sub> Si <sub>3</sub>		2,2-dichloro-4,4,6,6-tetramethylcyclotrisiloxane			
C <sub>4</sub> H <sub>12</sub> Cl <sub>4</sub> O <sub>4</sub> Si <sub>4</sub>	(SiO) <sub>4</sub> (CH <sub>3</sub> ) <sub>4</sub> Cl <sub>4</sub>	tetrachlorotetramethylcyclotetrasiloxane			
C <sub>4</sub> H <sub>12</sub> Cl <sub>6</sub> O <sub>3</sub> Si <sub>4</sub>	Si(CH <sub>3</sub> )Cl <sub>2</sub> OSi(CH <sub>3</sub> )[OSi(CH <sub>3</sub> )Cl <sub>2</sub> ]-OSi(CH <sub>3</sub> )Cl <sub>2</sub>	1,1,5,5-tetrachloro-3-[dichloro(methyl)silyloxy]-1,3,5-trimethyltrisiloxane			
C <sub>4</sub> H <sub>12</sub> O <sub>2</sub> Si <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> SiO-Si(CH <sub>3</sub> ) <sub>2</sub>	Tetramethylcyclodisiloxane			
C <sub>4</sub> H <sub>14</sub> OSi <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> HSiOSi(CH <sub>3</sub> ) <sub>2</sub> H	1,1,3,3-tetramethyldisiloxane	---	70	L, F, M
C <sub>6</sub> H <sub>16</sub> Br <sub>2</sub> OSi <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Br)SiOSi(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Br)	1,3-bis(bromomethyl)-1,1,3,3-tetramethyldisiloxane			CAS No. 2351-13-5
C <sub>6</sub> H <sub>16</sub> Cl <sub>2</sub> OSi <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Cl)SiOSi(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Cl)	1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane	---	204	M, I, F, flash point = 73 °C
C <sub>6</sub> H <sub>17</sub> ClOSi <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> Cl)SiOSi(CH <sub>3</sub> ) <sub>3</sub>	(chloromethyl)pentamethyldisiloxane			CAS No. 17201-83-1

TABLE 25. SILOXANES (continued).

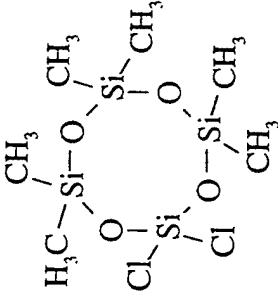
Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
$C_6H_{18}Cl_2O_2Si_3$	$(CH_3)_2ClSiOSi(CH_3)_2OSi(CH_3)_2Cl$	1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane	-53	184	
$C_6H_{18}Cl_2O_4Si_4$		2,2-dichloro-4,4,6,6,8,8-hexamethylcyclotetrasiloxane			
$C_6H_{18}OSi_2$	$(CH_3)_3SiOSi(CH_3)_3$	hexamethyldisiloxane	---	101	L, F, I, flash point = -2 °C
$C_6H_{18}OSi_2$	$(CH_3)(C_2H_5)HSiSi(CH_3)(C_2H_5)H$	1,3-diethyl-1,3-dimethyldisiloxane	-99	139	L, F, I
$C_6H_{18}O_3Si_3$	$(SiO)_3(CH_3)_6$	hexamethylcyclotrisiloxane	64	134	S, F, M
$C_8H_{21}ClOSi_2$	$(CH_3)_3SiOSi(CH_3)_2(CH_2CH_2CH_2Cl)$	(3-chloropropyl)pentamethyldisiloxane			
$C_8H_{22}Cl_2F_2O_3Si_4$	$(CH_3)_3SiOSi(CH_2Cl)FOSi(CH_2Cl)FOSi(CH_3)_3$	3,5-bis(chloromethyl)-3,5-difluoro-1,1,1,7,7,7-hexamethyltetrasiloxane			

TABLE 25. SILOXANES (continued).

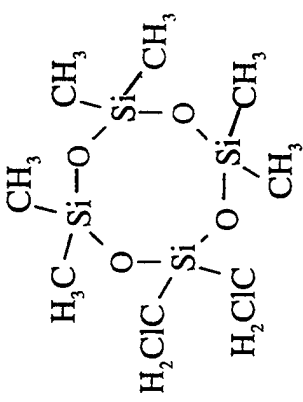
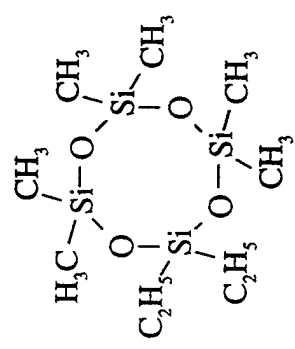
Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
$C_8H_{22}Cl_2O_4Si_4$		2,2-bis(chloromethyl)-4,4,6,6,8,8-hexamethylcyclotetrasiloxane			
$C_8H_{22}O_2Si_3$	$(CH_3)_3SiOSi(CH=CH_2)HOSi(CH_3)_3$	3-ethenyl-1,1,1,5,5,5-hexamethyltrisiloxane			
$C_8H_{22}O_3Si_2$	$Si(CH_3)_2(OC_2H_5)_2Si(CH_3)_2(OC_2H_5)_2$	1,3-diethoxy-1,1,3,3-tetramethyldisiloxane			
$C_8H_{22}O_5Si_2$	$(C_2H_5O)_2HSiOSi(C_2H_5O)_2H$	1,1,3,3-tetraethoxydisiloxane			CAS No. 18001-60-0
$C_8H_{22}O_5Si_3$		2,2-diethoxy-4,4,6,6-tetramethylcyclotrisiloxane			



TABLE 25. SILOXANES (continued).

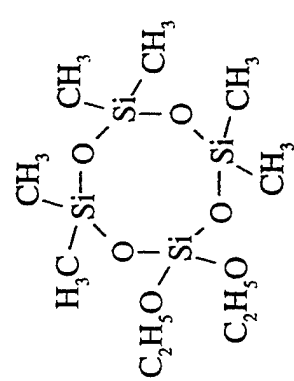
Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
$C_8H_{23}BrO_4Si_4$	$(SiO)_4(CH_3)_7(CH_2Br)$	(bromomethyl)heptamethylcyclotetra-siloxane			
$C_8H_{23}ClO_2Si_3$	$(CH_3)_3SiOSi(CH_3)(CH_2Cl)-OSi(CH_3)_3$	3-(chloromethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane			
$C_8H_{23}ClO_4Si_4$	$(SiO)_4(CH_3)_7(CH_2Cl)$	(chloromethyl)heptamethylcyclotetra-siloxane			
$C_8H_{24}Cl_2O_3Si_4$	$(CH_3)_2ClSiOSi(CH_3)_2OSi(CH_3)_2O-Si(CH_3)_2Cl$	1,7-dichlorooctamethyltetrasiloxane	-62	222	C
$C_8H_{24}O_2Si_3$	$(CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3$	octamethyltrisiloxane	≈-80	153	L, F, M
$C_8H_{24}O_4Si_4$	$(SiO)_4(CH_3)_8$	octamethylcyclotetrasiloxane	17	175	M
$C_{10}H_{28}Cl_2O_3Si_4$	$(CH_3)_2(CH_2Cl)SiOSi(CH_3)_2O-Si(CH_3)_2OSi(CH_3)_2(CH_2Cl)$	1,7-bis(chloromethyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane			
$C_{10}H_{28}O_6Si_4$		2,2-diethoxy-4,4,6,8,8-hexamethylcyclotetrasiloxane			

TABLE 25. SILOXANES (continued).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
$C_{10}H_{29}ClO_3Si_4$	$(CH_3)_3SiOSi(CH_2Cl)[OSi(CH_3)_3]O-Si(CH_3)_3$	3-(chloromethyl)-1,1,1,5,5,5-hexamethyl-3-[(trimethylsilyl)oxy]trisilane			
$C_{10}H_{30}Cl_2O_6Si_6$		2,6-dichloro-2,4,4,6,8,10,10,12,12-decamethylcyclohexasiloxane			
$C_{10}H_{30}O_3Si_4$	$(CH_3)_3Si[OSi(CH_3)_2]_2OSi(CH_3)_3$	decamethyltetrasiloxane	-70	194	F, T
$C_{10}H_{30}O_5Si_5$		2,4,6,8,10-pentaethylcyclopentasiloxane	-38	210	

TABLE 25. SILOXANES (concluded).

Empirical formula	Structural formula	Name	MP, °C	BP, <sup>a</sup> °C	Notes <sup>b</sup>
C <sub>12</sub> H <sub>36</sub> O <sub>4</sub> Si <sub>5</sub>	Si(CH <sub>3</sub> ) <sub>3</sub> [OSi(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>	dodecamethylpentasiloxane	-80	229	
C <sub>12</sub> H <sub>36</sub> O <sub>6</sub> Si <sub>6</sub>	(SiO) <sub>6</sub> (CH <sub>3</sub> ) <sub>12</sub>	dodecamethylcyclohexasiloxane	-3	245	
C <sub>14</sub> H <sub>42</sub> O <sub>5</sub> Si <sub>6</sub>	CH <sub>3</sub> [(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>5</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	tetradecamethylhexasiloxane	<-100	142 (20)	
C <sub>14</sub> H <sub>42</sub> O <sub>7</sub> Si <sub>7</sub>	[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>7</sub>	tetradecamethylcycloheptasiloxane	-26	154 (20)	
C <sub>16</sub> H <sub>48</sub> O <sub>6</sub> Si <sub>7</sub>	CH <sub>3</sub> [(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>6</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	hexadecamethylheptasiloxane	≈-80	190	
C <sub>16</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>8</sub>	[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>8</sub>	hexadecamethylcyclooctasiloxane	≈-80	175 (20)	
C <sub>18</sub> H <sub>54</sub> O <sub>9</sub> Si <sub>9</sub>	[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>9</sub>	octadecamethylcyclononasiloxane		≈188	

<sup>a</sup>Boiling points are at 1 atmosphere (760 Torr) except where values in parentheses give the pressure (in Torr).<sup>b</sup>L = liquid, S = solid, F = flammable, I = irritant, C = corrosive, T = toxic, M = decomposes in moist air.

## F. SILOXANES CONTAINING BROMOCARBON AND/OR FLUOROCARBON SUBSTITUENTS

A computer search of the American Chemical Society (ACS) Chemical Abstracts database for siloxanes containing bromocarbon and/or fluorocarbon substituent groups attached to silicon was made. Groups containing sulfur, nitro groups, and phosphorus have been ignored. The substituents found are shown in Table 26; a list of many of the structures found containing those substituents is presented in Table 27. The latter table omits polymeric compounds, compounds containing metals, several very large molecular weight compounds, and sulfur compounds. Each substituent group has been assigned a label to conserve space and to better identify the group in the structures shown in Table 27.

Very few bromine-containing substituents have been reported for siloxanes. The only ones found in the computerized search performed here are  $-\text{CHBrCH}_2\text{CF}_2\text{CBrF}_2$  (R4),  $-\text{CH}_2\text{CH}_2\text{CClFCBrF}_2$  (R7), and  $-\text{CH}_2\text{CH}_2\text{CF}_2\text{BrCF}_2$  (R11). All of these have longer chains than desirable. More appropriate would be some of the bromine-containing substituents found for the silanes, in particular  $-\text{CH}_2\text{Br}$  (B2),  $-\text{CHBrCl}$  (B4),  $-\text{CHBr}_2$  (B11),  $-\text{CHBrF}$  (B32), and  $-\text{CBr}_2\text{F}$  (B33) (Table 14). On the other hand, a relatively large number of fluorine-containing substituents have been reported for siloxanes, possibly more than for the silanes. Of particular interest are  $-\text{CF}_3$  (R1),  $-\text{OCH}_2\text{CF}_3$  (R51), and  $-\text{CH}_2\text{CH}_2\text{CF}_3$  (R5). An extremely large number of siloxanes containing the last substituent have been reported (Table 26 and Table 27). Some of the unsaturated groups such as  $-\text{CF}=\text{CF}_2$  (R2),  $-\text{OCH}=\text{C}(\text{CF}_3)_2$  (R3),  $-\text{C}(\text{CF}_3)=\text{CF}_2$  (R20),  $-\text{CH}_2\text{CH}=\text{CF}_2$  (R63), and  $-\text{CH}=\text{CHCF}_3$  (R73) could provide excellent sites for introduction of bromine into a siloxane.

TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES.

Group label	Structural formula	CAS No. of parent compound		
R1	-CF <sub>3</sub>		115829-54-4	
			53208-16-5	
			<sup>a</sup> 164082-23-9	
			<sup>a</sup> 161627-90-3	
			54484-30-9	
			129933-13-7	
R2	-CF=CF <sub>2</sub>		5721-28-8	
R3	-OCH=C(CF <sub>3</sub> ) <sub>2</sub>		17156-44-4	
			17156-45-5	
R4	-CHBrCH <sub>2</sub> CF <sub>2</sub> CBrF <sub>2</sub>		113688-45-5	
R5	-CH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	71864-54-5	167274-59-1	28550-30-3
		69288-21-7	<sup>a</sup> 162023-57-6	23296-32-4
		64339-48-6	156849-44-4	23174-01-8
		60608-14-2	142174-47-8	23173-99-1
		59485-25-5	141901-57-7	20442-93-7
		54686-33-8	141901-56-6	15732-55-5
		41291-20-7	141901-58-8	15445-52-0
		38916-86-8	141901-59-9	13092-31-4
		92531-92-5	109961-44-6	6892-36-0
		83900-17-8	97731-09-4	5827-39-4
		83931-83-2	96125-68-7	2939-62-0
		62117-18-4	37593-06-3	2810-64-2
		167274-56-8	31922-67-5	2652-37-1
		173262-57-2	31922-66-4	2374-18-7
		<sup>a</sup> 169116-95-4	31922-65-3	2284-41-5
		96125-65-4	28886-09-1	2070-79-3
		96037-63-7	1185-66-6	660-00-4
		95735-70-9	867-06-1	461-00-7
		154702-68-8	690-56-2	429-67-4
		28364-07-0	406-61-1	
R6	-CH <sub>2</sub> CH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>		71363-69-4	
			503-43-5	
R7	-CH <sub>2</sub> CH <sub>2</sub> CClFCBrF <sub>2</sub>		5674-89-5	

TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES (continued).

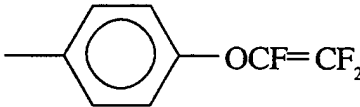
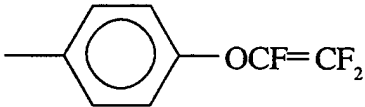
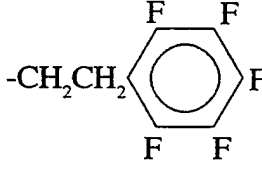
Group label	Structural formula	CAS No. of parent compound
R8	$\begin{array}{c} \text{CF}_3 \\ \diagup \\ \text{---CH} \\ \diagdown \\ \text{CH}_3 \end{array}$	85279-86-3 84841-30-5
R9	$\text{---CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	122179-35-5 147946-67-6 104745-17-7
R10		172703-20-7
R11	$\text{---CH}_2\text{CH}_2\text{CF}_2\text{CBrF}_2$	32834-89-2
R12		113358-14-8
R13		120347-86-6 111133-53-0 36253-28-8 13235-89-7
R14	$\text{---CH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_3$	169116-94-3
R15	$\text{---CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	<sup>a</sup> 169116-93-2 167648-69-3 <sup>ab</sup> 165688-91-5 <sup>b</sup> 165688-85-7 164254-89-1 1162920-45-8 147011-63-0 147011-62-9 142860-62-6 139415-46-6 134251-03-9 133068-44-7 62149-39-7
R16	$\text{---CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_3$	167648-68-2
R16	$\text{---CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_3$	167648-68-2

TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES (continued).

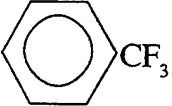
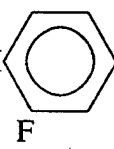
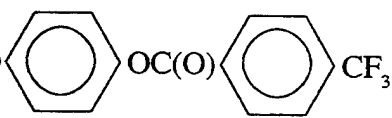
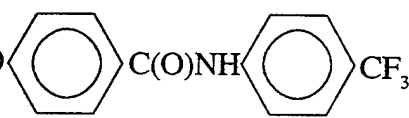
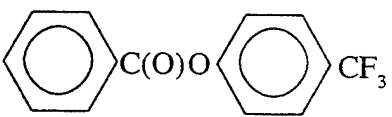
Group label	Structural formula	CAS No. of parent compound
R16	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_3$	167648-68-2
R17	$\text{---CH}_2\text{CH}_2\text{CH}_2\text{NHC(=NH)NHC(=NH)NH}$ 	<sup>a</sup> 167425-96-9
R18	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3$	167274-59-1
R19	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_3$	162920-44-7
R20	$-\text{C}(\text{CF}_3)=\text{CF}_2$	<sup>a</sup> 161627-90-3
R21	$-\text{OCH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	159835-46-8
R22	$-\text{OCH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	159835-45-7
R23	$-\text{OCH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$	159835-44-6
R24	$-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	156359-91-0
R25	$-\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCF}_2\text{CHF}_2$	156359-88-5
R26	$-\text{CH}_2\text{CH}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_3$	150214-96-3 150214-95-2 147011-64-1
R27	$\text{---NH}$ 	146033-63-8
R28	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_3$	144885-21-2
R29	$\text{---CH}_2\text{O}$ 	144386-06-1
R30	$\text{---CH}_2\text{O}$ 	144386-02-7
R31	$\text{---CH}_2\text{O}$ 	144386-01-6

TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES (continued).

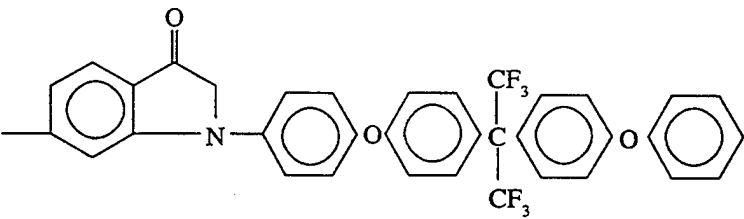
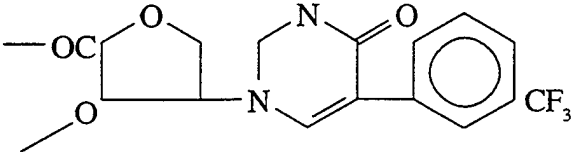
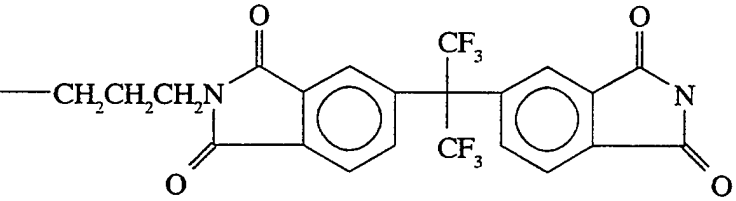
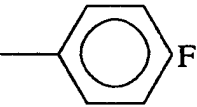
Group label	Structural formula	CAS No. of parent compound
R32	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	<sup>a</sup> 141634-95-9 133068-42-5 94237-17-9
R33		139604-00-5
R34	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}(\text{CH}_3)\text{OCF}_2\text{CF}_2\text{CF}_3$	134251-04-0
R35	$-\text{CHF}_2$	132998-67-5
R36		129507-85-3
R37	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_3$	129498-27-7
R38		<sup>a</sup> 129316-98-9
R39		128903-25-3 101805-60-1 4308-97-8 2871-21-8 2287-69-6 78164-70-2
R40	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{O})\text{CF}_3$	128254-71-7
R41	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_2\text{CHF}_2$	111731-16-9 111731-15-8
R42	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$	111731-14-7 111731-11-1



TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES (continued).

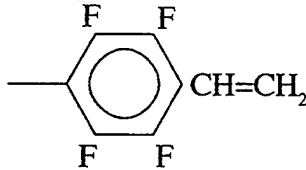
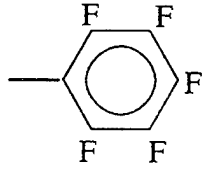
Group label	Structural formula	CAS No. of parent compound
R43	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$	111731-13-6
R44	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_2\text{CHF}_2$	111731-12-5
R45	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	111133-53-0 111133-52-9
R46	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_2\text{CCl}_2\text{F}$	111133-48-3
R47	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3$	111133-47-2
R48	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CHFCF}_3$	111133-46-1
R49	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OC(O)CH=CHC(O)OCH}_2\text{CF}_3$	109998-09-6
R50	$  \begin{array}{c}  \text{F} \\    \\  \text{H}_2\text{C}-\text{C}-\text{F} \\    \quad   \\  -\text{CH}-\text{C}-\text{Cl} \\    \\  \text{F}  \end{array}  $	109651-61-8
R51	$-\text{OCH}_2\text{CF}_3$	106836-33-3
R52		99794-57-7
R53	$-(\text{CH}_2)_{25}\text{CF}_3$	96049-21-7
R54	$-\text{Cl}=\text{CHCF}_2\text{CF}_2\text{CF}_3$	83261-95-4
R55	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OC(O)CF}_3$	72838-51-8 1510-50-5
R56		71338-88-0 63107-85-7 63107-84-6 63107-83-5 63107-81-3 20124-26-9 20124-24-7 19091-32-8

TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES (continued).

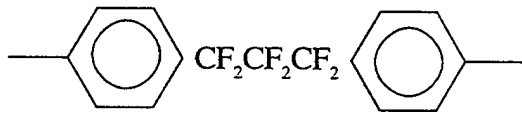
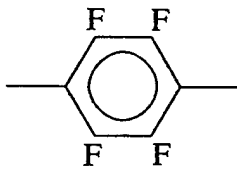
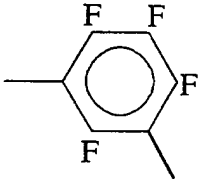
Group label	Structural formula	CAS No. of parent compound
R57	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{CF}_3$	70105-66-7
R58	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2-$	64339-48-6
R59	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$	63263-62-7
R60	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CF}_2\text{CHF}_2$	63263-61-6
R61	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCF}(\text{CF}_3)_2$	56153-69-6 56153-68-5
R62	$-\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{OCH}(\text{CF}_3)_2$	55629-41-9
R63	$-\text{CH}_2\text{CH}=\text{CF}_2$	53980-28-2
R64	$\begin{array}{c} \text{CH}_2 \\ / \quad \backslash \\ -\text{CH}-\text{CF}_2 \end{array}$	53315-75-6 53315-74-5
R65	$-\text{CH}_2\text{OC}(\text{O})\text{CF}_3$	53214-08-7
R66		<sup>a</sup> 51345-13-2
R67	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2-$	41291-20-7
R68	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$	38916-86-8
R69	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{OCF}(\text{CF}_3)_2$	36387-48-1
R70		26323-18-2 19091-30-6
R71	$-\text{C}_6\text{ClF}_4$	25704-69-2
R72		25459-27-2
R73	$-\text{CH}=\text{CHCF}_3$	17913-07-4

TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES (continued).

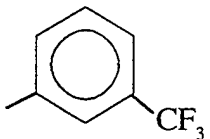
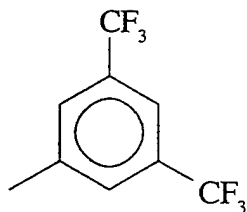
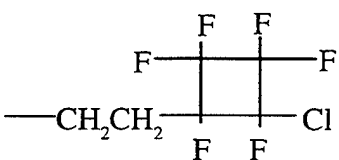
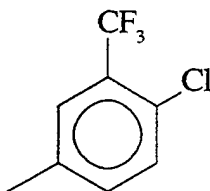
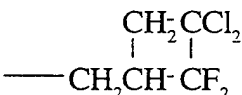
Group label	Structural formula	CAS No. of parent compound
R74		17658-72-9 2127-57-3
R75	$-\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_3$	16165-56-3
R76	$-\text{CH}_2\text{CH}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{CF}_3$	15445-51-9 10366-28-6
R77	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	5674-92-0
R78	$-\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	5674-90-8
R79		4123-91-5
R80	$-\text{CH}_2\text{CH}_2\text{CHF}_2$	3109-59-9
R81		2803-17-0
R82		2560-94-3 2127-52-8
R83	$-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3$	1995-95-5
R84	$\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CF}_2\text{CHF}_2$	674-19-1
R85		565-58-2

TABLE 26. FLUOROORGANIC AND BROMOORGANIC SUBSTITUENTS  
IN SILOXANES (concluded).

Group label	Structural formula	CAS No. of parent compound
R86	$\text{CH}_2\text{CH}(\text{CH}_3)\text{CF}_3$	503-42-4
R87	$\begin{array}{c} \text{CH}_2\text{CF}_2 \\   \quad   \\ \text{—CH—CF}_2 \end{array}$	338-86-3

<sup>a</sup>CAS No. is for polymeric structure.

<sup>b</sup>Contains transition metal.

<sup>c</sup>Isomer not specified.

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS.

Empirical formula	Structural formula	Name	CAS No.
$C_2H_6F_4OSi_2$	$(R35)H_2SiOSiH_2(R35)$	1,3-bis(difluoromethyl)disiloxane	132998-67-5
$C_2H_6F_6O_4Si_4$	$^a[(R1)HSiO]_2(OSiH_2)_2$	bis(trifluoromethyl)-cyclo-tetrasiloxane	115829-54-4
$C_2F_{10}OSi_2$	$(R1)F_2SiOSiF_2(R1)$	1,1,3,3-tetrafluoro-1,3-bis(trifluoromethyl)disiloxane	54484-30-9
$C_8H_{11}F_5OSi_3$	$(R56)(CH_3)_2Si-SiH_2OSiH_3$	[dimethyl(pentafluorophenyl)silyl]-disiloxane	71338-88-0
$C_8H_{12}Cl_2F_4OSi_2$	$(R64)(CH_3)ClSiOSiCl(CH_3)(R64)$	1,3-dichloro-1,3-bis(2,2-difluorocyclopropyl)-1,3-dimethyldisiloxane	53315-75-6
$C_8H_{12}F_6OSi_2$	$(R2)(CH_3)_2SiOSi(CH_3)_2(R2)$	1,1,3,3-tetramethyl-1,3-bis(trifluorovinyl)disiloxane	5721-28-8
$C_8H_{12}F_{12}O_4Si_4$	$[(CH_3)(R1)SiO]_4$	1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trifluoromethyl)-cyclo-tetrasiloxane	53208-16-5
$C_8H_{14}F_6O_2Si_2$	$(R3)(CH_3)_2SiOSiH(CH_3)_2$	1,1,3,3-tetramethyl-1-[[3,3,3-trifluoro-2-(trifluoromethyl)propenyl]oxy]-disiloxane	17156-44-4
$C_8H_{16}F_6OSi_2$	$(R5)(CH_3)HSiOSiH(CH_3)(R5)$	1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane	54686-33-8
$C_8H_{16}F_6O_3Si_2$	$(R8)(CH_3)(HO)SiOSi(OH)(CH_3)(R8)$	1,3-dimethyl-1,3-bis(2,2,2-trifluoro-1-methylethyl)-1,3-disiloxanediol	84841-30-5

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_8H_{18}F_3O_4Si_4$	$-(R1)(CH_3)SiO(CH_3)_2SiO(CH_3)_2SiO(CH_3)_2SiO-$	heptamethyl(trifluoromethyl)-cyclo-tetrasiloxane	129933-13-7
$C_8H_{21}F_3O_2Si_3$	$(R5)(CH_3)_2SiO(CH_3)_2SiOSi(CH_3)_2(R5)$	1,1,3,5,5-pentamethyl-1-3-(3,3,3-trifluoropropyl)trisiloxane	28364-07-0
$C_{10}H_{16}F_6O_5Si_2$	$(R65)(CH_3)_2SiOSi(CH_3)_2(R65)$	(1,1,3,3-tetramethyl-1,3-disiloxanediy)bis(methylene) ester of trifluoroacetic acid	53214-08-7
$C_{10}H_{16}F_7IOSi_2$	$(R54)(CH_3)_2SiOSi(CH_3)_3$	(3,3,4,4,5,5-heptafluoro-1-iodo-1-pentenyl)pentamethyldisiloxane	83261-95-4
$C_{10}H_{17}F_9OSi_2$	$(R9)(CH_3)_2SiOSiH(CH_3)_2$	1,1,3,3-tetramethyl-1-(3,3,4,4,5,5,6,6-nonafluorohexyl)disiloxane	104745-17-7
$C_{10}H_{18}F_4OSi_2$	$(R63)(CH_3)_2SiOSi(CH_3)_2(R63)$	1,3-bis(3,3-difluoro-2-propenyl)-1,1,3,3-tetramethyldisiloxane	53980-28-2
$C_{10}H_{18}F_4OSi_2$	$(R64)(CH_3)_2SiOSi(CH_3)_2(R64)$	1,3-bis(2,2-difluorocyclopropyl)-1,1,3,3-tetramethyldisiloxane	53315-74-5
$C_{10}H_{20}Br_2F_4OSi_2$	$CH_2=CHSi(CH_3)_2OSi(CH_3)_2(R4)$	1-(1-4-dibromo-3,3,4,4-tetrafluorobutyl)-3-ethenyl-1,1,3,3-tetramethyldisiloxane	113688-45-5
$C_{10}H_{20}F_6O_5Si_2$	$(R5)(OCH_3)_2SiOSi(OCH_3)_2(R5)$	1,1,3,3-tetramethoxy-1,3-bis(3,3,3-trifluoropropyl)disiloxane	109961-44-6
$C_{10}H_{22}F_6O_4Si_4$	$[OSiH(CH_3)OSi(CH_3)(R5)]_2$	2,4,6,8-tetramethyl-2,6-bis(3,3,3-trifluoropropyl)cyclo-tetrasiloxane	154702-68-8

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{10}H_{22}F_6O_4Si_4$	$-(R5)(CH_3)SiO(R5)(CH_3)SiO(CH_3)HSiO(CH_3)HSiO-$	2,4,6,8-tetramethyl-2,4-bis(3,3,3-trifluoropropyl)cyclotetrasiloxane	62117-18-4
$C_{11}H_{13}Cl_2F_{13}OSi_2$	$(R32)SiCl_2OSi(CH_3)_3$	1,1-dichloro-3,3,3-trimethyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)disiloxane	94237-17-9
$C_{11}H_{15}F_5OSi_2$	$(R56)(CH_3)_2SiOSi(CH_3)_3$	pentamethyl(pentafluorophenyl)disiloxane	63107-85-7
$C_{11}H_{19}F_9OSi_2$	$(R5)_3SiOSiH(CH_3)_2$	3,3-dimethyl-1,1,1-tris(3,3,3-trifluoropropyl)disiloxane	59485-25-5
$C_{12}H_{12}F_{10}O_7Si_2$	${}^b(R57)Si(O)OSi(O)(R57)$	${}^b$ 1,3-dioxo-1,3-disiloxanediyldi-3,1-propanediyl ester of pentafluoropropanoic acid	70105-66-7
$C_{12}H_{17}F_{13}OSi_2$	$(R32)(CH_3)_2SiOSiH(CH_3)_2$	1,1,3,3-tetramethyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)disiloxane	133068-42-5
$C_{12}H_{18}F_8OSi_2$	$(R87)(CH_3)_2SiOSi(CH_3)_2(R87)$	1,1,3,3-tetramethyl-1,3-bis(2,2,3,3-tetrafluorocyclobutyl)disiloxane	338-86-3
$C_{12}H_{20}Br_2Cl_2F_6OSi_2$	$(R7)(CH_3)_2SiOSi(CH_3)_2(R7)$	1,3-bis(4-bromo-3-chloro-3,4,4-trifluorobutyl)-1,1,3,3-tetramethyl-disiloxane	5674-89-5
$C_{12}H_{20}F_6OSi_2$	$(R78)CH_3)_2SiOSi(CH_3)_2(R78)$	1,1,3,3-tetramethyl-1,3-bis(3,4,4-trifluoro-3-butenyl)disiloxane	5674-90-8

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{12}H_{20}F_{10}OSi_2$	$(R6)(CH_3)_2SiOSi(CH_3)_2(R6)$	1,1,3,3-tetramethyl-1,3-bis(3,3,4,4,4-pentafluorobutyl)disiloxane	71363-69-4
$C_{12}H_{22}F_6O_4Si_4$	$[(R73)(CH_3)SiOSi(CH_3)_2O]_2$	2,2,4,6,6,8-hexamethyl-4,8-bis(3,3,3-trifluoropropenyl)cyclotetrasiloxane	17913-07-4
$C_{12}H_{24}F_6OSi_2$	$(R5)(CH_3)(C_2H_5)SiOSi(CH_3)(C_2H_5)(R5)$	1,3-diethyl-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane	167274-56-8
$C_{12}H_{24}F_6OSi_2$	$(R5)(CH_3)(C_2H_5)SiOSi(CH_3)_2(R18)$	1ethyl-1,3,3-trimethyl-3-(4,4,4-trifluorobutyl)-1-(3,3,3-trifluoropropyl)disiloxane	167274-59-1
$C_{13}H_{18}F_4OSi_2$	$(R52)(CH_3)_2SiOSi(CH_3)_3$	(4-ethenyl-2,3,5,6-tetrafluorophenyl)-pentamethyl-disiloxane	99794-57-7
$C_{13}H_{21}F_{11}O_3Si_2$	$(R37)(CH_3)_2SiOSiH(CH_3)_2$	1,1,3,3-tetramethyl-1-[3-[2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propoxy]propyl]disiloxane	129498-27-7
$C_{13}H_{30}F_4O_5Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R41)-$	heptamethyl[3-(2,2,3,3-tetrafluoropropoxy)propyl]-cyclotetrasiloxane	111731-15-8
$C_{14}H_{17}F_{17}OSi_2$	$(R15)(CH_3)_2SiOSiH(CH_3)_2$	1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptaecafluorodecyl)-1,1,3,3-tetramethyl-disiloxane	133068-44-7



TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{14}H_{18}Cl_2F_{14}O_3Si_2$	$(R61)(CH_3)ClSiOSiCl(CH_3)(R61)$	1,3-dichloro-1,3-dimethyl-1,3-bis[3-[1,2,2-tetrafluoro-1-(trifluoromethyl)-ethoxy]propyl]disiloxane	56153-68-5
$C_{14}H_{19}F_{17}O_4Si_4$	$-OSiH(CH_3)OSiH(CH_3)OSiH(CH_3)OSi(CH_3)(R15)-$	2-(3,3,4,4,4,5,6,6,7,7,8,8,9,10,10,10-heptadecafluorodecyl)-2,4,6,8-tetramethylcyclotetrasiloxane	147011-62-9
$C_{14}H_{19}F_{17}O_6Si_4$	$-OSiH(CH_3)OSiH(CH_3)OSiH(CH_3)OSi(CH_3)(R26)-$	2,4,6,8-tetramethyl-2-[3,4,4,4-tetrafluoro-3-[1,1,2,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]butyl]cyclotetrasiloxane	147011-64-1
$C_{14}H_{20}F_{14}O_5Si_2$	$(R61)(CH_3)(HO)SiOSi(OH)(CH_3)(R61)$	1,3-dimethyl-1,3-bis[3-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethoxy]propyl]-1,3-disiloxanediol	56153-69-6
$C_{14}H_{22}Cl_4F_4OSi_2$	$(R85)(CH_3)_2SiOSi(CH_3)_2(R85)$	1,3-bis[(3,3-dichloro-2,2-difluorocyclobutyl)methyl]-1,1,3,3-tetramethyldisiloxane	565-58-2
$C_{14}H_{24}Cl_2F_6O_4Si_4$	$-OSi(CH_3)_2OSi(CH_3)(R50)OSi(CH_3)_2OSi(CH_3)(R50)-$	bis(2-chloro-2,3,3-trifluorocyclobutyl)hexamethylcyclotetrasiloxane	109651-61-8
$C_{14}H_{24}F_6OSi_2$	$(R77)(CH_3)_2SiOSi(CH_3)_2(R77)$	1,1,3,3-tetramethyl-1,3-bis(4,5,5-trifluoro-4-pentenyl)disiloxane	5674-92-0

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{14}H_{26}F_6N_2O_3Si_2$	$(R40)(CH_3)_2SiOSi(CH_3)_2(R40)$	N,N'-[(1,1,3,3-tetramethyl-1,3-disiloxanediy)di-3,1-propanediyl]bis[2,2,2-trifluoroacetamide]	128254-71-7
$C_{14}H_{28}F_6O_3Si_2$	$(R47)(CH_3)_2SiOSi(CH_3)_2(R47)$	1,1,3,3-tetramethyl-1,3-bis[3-(2,2,2-trifluoroethoxy)propyl]disiloxane	111133-47-2
$C_{14}H_{32}F_6O_3Si_4$	$(CH_3)_3SiOSi(CH_3)(R5)OSi(CH_3)(R5)OSi(CH_3)_3$	1,1,1,3,5,7,7,7-octamethyl-3,5-bis(3,3,3-trifluoropropyl)tetrasiloxane	62149-39-7
$C_{15}H_4F_{17}N_5O_6Si_2$	$(OCN)_3SiOSi(NCO)_2(R15)$	1-(3,3,4,4,5,5,6,6,7,7,8,8,9,10,10,10-heptadecafluorodecyl)-1,1,3,3,3-pentaisocyanatodisiloxane	164254-89-1
$C_{15}H_{23}F_{13}O_2Si_2$	$(R45)(CH_3)_2SiOSiH(CH_3)_2$	1,1,3,3-tetramethyl-1-[3-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]propyl]-disiloxane	111133-52-9
$C_{15}H_{30}F_8O_5Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R42)-$	heptamethyl[3-[(2,2,3,3,4,4,5,5-octafluoropentyl)oxy]propyl]-cyclo-tetrasiloxane	111731-14-7
$C_{16}H_{12}Cl_2F_8OSi_2$	$(R71)(CH_3)_2SiOSi(CH_3)_2(R71)$	1,3-bis(chlorotetrafluorophenyl)-1,1,3,3-tetramethyldisiloxane	25704-69-2
$C_{16}H_{20}Cl_2F_{12}OSi_2$	$(R81)(CH_3)_2SiOSi(CH_3)_2(R81)$	1,3-bis[2-(2-chloro-1,2,3,3,4,4-hexafluorocyclobutyl)ethyl]-1,1,3,3-tetramethyldisiloxane	2803-17-0

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{16}H_{20}F_{14}O_7Si_2$	$(R62)(CH_3)_2SiOSi(CH_3)_2(R62)$	(1,1,3,3-tetramethyl-1,3-disiloxanediy)bis(methylene) ester of [1,2,2,2-tetrafluoro-1-(trifluoromethylethoxy)acetic acid	55629-41-9
$C_{16}H_{20}F_{18}OSi_2$	$(R9)(CH_3)_2SiOSi(CH_3)_2(R9)$	1,1,3,3-tetramethyl-1,3-bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)disiloxane	122179-35-5
$C_{16}H_{26}F_{12}O_3Si_2$	$(R48)(CH_3)_2SiOSi(CH_3)_2(R48)$	1,3-bis[3-(1,1,2,3,3,3-hexafluoropropoxy)propyl]-1,1,2,2-tetramethyldisiloxane	111133-46-1
$C_{16}H_{28}Cl_4F_6O_3Si_2$	$(R46)(CH_3)_2SiOSi(CH_3)_2(R46)$	1,3-bis[3-(3,3-dichloro-2,2,3-trifluoropropoxy)propyl]-1,1,3,3-tetramethyldisiloxane	111133-48-3
$C_{16}H_{28}F_6O_5Si_2$	$(R55)(CH_3)_2SiOSi(CH_3)_2(R55)$	(1,1,3,3-tetramethyl-1,3-disiloxanediy)di-4,1-butanediyl ester of trifluoroacetic acid	72838-51-8
$C_{16}H_{28}F_{12}O_4Si_4$	$[(R8)(CH_3)SiO]_4$	2,4,6,8-tetramethyl-2,4,6,8-tetrakis(2,2,2-trifluoro-1-methylethyl)cyclotetrasiloxane	85279-86-3
$C_{16}H_{28}F_{12}O_4Si_4$	$[(R5)(CH_3)SiO]_4$	2,4,6,8-tetramethyl-2,4,6,8-tetrakis(3,3,3-trifluoropropyl)cyclotetrasiloxane	<sup>c</sup> 141901-57-7 141901-56-6 141901-58-8 141901-59-9

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{16}H_{32}F_8O_4Si_4$	$[(R80)(CH_3)SiO]_4$	2,4,6,8-tetrakis(3,3-difluoropropyl)- 2,4,6,8-tetramethylcyclotetrasiloxane	3109-59-9
$C_{16}H_{34}F_4O_8Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R25)-$	2,4,4,6,6,8,8-heptamethyl-2- hydroxy-3-(1,1,2,2- tetrafluoroethoxy)propyl ester of cyclotetrasiloxanepropanoic acid	156359-88-5
$C_{16}H_{40}F_6O_7Si_6$	$(R51)(CH_3)_2Si[OSi(CH_3)_2]_4OSi(CH_3)_2(R51)$	1,1,3,3,5,5,7,7,9,9,11,11- dodecamethyl-1,11-bis(2,2,2- trifluoroethoxy)hexasiloxane	106836-33-3
$C_{17}H_{24}F_6OSi_2$	$(R5)(CH_3)_2SiOSi(CH_3)(C_6H_4CH=CH_2)(R5)$	1-(4-ethenylphenyl)-1,3,3-trimethyl- 1,3-bis(3,3,3- trifluoropropyl)disiloxane	97731-09-4
$C_{17}H_{30}F_{12}O_5Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R43)-$	$[3-[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy]propyl]-$ heptamethylcyclotetrasiloxane	111731-13-6
$C_{17}H_{31}F_9O_8Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R24)-$	2,4,4,6,6,8,8-heptamethyl-2- hydroxy-3-(nonafluorobutoxy)propyl ester of cyclotetrasiloxanepropanoic acid	156359-91-0
$C_{17}H_{25}F_{17}O_4Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R15)-$	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10- heptadecafluorodecyl)heptamethyl- cyclotetrasiloxane	142860-62-6

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{18}H_{23}F_9O_2Si_2$	$(R23)(CH_3)_2SiOSi(CH_3)_2(C_6H_4CH=CH_2)$	1-(4-ethenylphenyl)-1,1,3,3-tetramethyl-3-[(3,3,4,4,5,5,6,6,6-tridecafluorooctyl)oxy]disiloxane	159835-44-6
$C_{18}H_{24}F_{18}OSi_2$	$(R5)_3SiOSi(R5)_3$	hexakis(3,3,3-trifluoropropyl)disiloxane	1185-66-6
$C_{19}H_{27}F_{19}O_7Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R14)-$	[3-[1,1,2,3,3,3-hexafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]propyl]-heptamethylcyclotetrasiloxane	169116-94-3
$C_{18}H_{28}F_{14}O_3Si_2$	$(R5)(R68)(CH_3)_2SiOSi(CH_3)(R68)(R_5)$	5,5'-[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-1,3-disiloxanediy]bis[2,2,3,3-tetrafluoro-1-pentanol]	38916-86-8
$C_{18}H_{32}F_{12}O_4Si_4$	$-(R76)(CH_3)_2SiO(R76)(CH_3)_2SiO(CH_3)_2SiO(CH_3)_2SiO-$	2,2,4,4,6,8-hexamethyl-6,8-bis[5,5,5-trifluoro-2-(trifluoromethyl)pentyl]-cyclotetrasiloxane	15445-51-9
$C_{18}H_{36}F_8O_6Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R44)OSi(CH_3)(R44)-$	2,2,4,4,6,8-hexamethyl-6,8-bis[3-(2,2,3,3-tetrafluoropropoxy)propyl]-cyclotetrasiloxane	111731-12-5
$C_{18}H_{36}F_{10}O_2Si_4$	$(R5)(CH_3)[H(CH_3)_2SiO]Si(R58)Si[OSi(CH_3)_2H]-(CH_3)(R5)$	1,1'-(3,3,4,4-tetrafluoro-1,6-hexanediy)bis[1,3,3-trimethyl-1-(3,3,3-trifluoropropyl)disiloxane]	64339-48-6

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{19}H_{36}F_8O_8Si_4$	$-OSiH(CH_3)OSiH(CH_3)OSi(R34)OSi(CH_3)_2-{(CH_2)_3OCH_2CH^OCH_2}-$	2-[3-[2-fluoro-2-(heptafluoropropoxy)propoxy]-propyl]-2,4,6,8-tetramethyl-4-[3-oxiranylmethoxy]propyl]-cyclo-tetrasiloxane	134251-04-0
$C_{19}H_{40}BrFOSi_5$	$(R12)\{C[Si(CH_3)_3]_3\}FSiOSi(CH_3)_3$	1-(4-bromophenyl)-1-fluoro-3,3,3-trimethyl-1-[tris(trimethylsilyl)methyl]disiloxane	113358-14-8
$C_{20}H_{20}F_6O_3Si_2$	$(R10)(CH_3)_2SiOSi(CH_3)_2(R10)$	1,1,3,3-tetramethyl-1,3-bis[4-[(trifluoroethenyl)oxy]phenyl]-disiloxane	172703-20-7
$C_{20}H_{23}F_{13}O_2Si_2$	$(R22)(CH_3)_2SiOSi(CH_3)_2(C_6H_4CH=CH_2)$	1-(4-ethenylphenyl)-1,1,3,3-tetramethyl-3-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]disiloxane	159835-45-7
$C_{20}H_{24}F_{10}O_3Si_4$	$(R56)(CH_3)_2Si[O(CH_3)_2Si]_2OSi(CH_3)_2(R56)$	1,1,3,3,5,5,7,7-octamethyl-1,7-bis(pentafluorophenyl)tetrasiloxane	63107-81-3
$C_{20}H_{25}F_{17}O_4Si_4$	$-Si(CH_3)(CH=CH_2)OSi(CH_3)(CH=CH_2)OSi(CH_3)-(CH=CH_2)OSi(CH_3)(R15)O-$	2,4,6-triethenyl-8-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-2,4,6,8-tetramethylcyclo-tetrasiloxane	167648-69-3

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{20}H_{28}Br_4F_{16}O_4Si_4$	$[Si(CH_3)(R11)]_4$	2,4,6,8-tetrakis(4-bromo-3,3,4,4-tetrafluorobutyl)-2,4,6,8-tetramethylcyclotetrasiloxane	32834-89-2
$C_{20}H_{28}F_{14}O_7Si_2$	$(R69)(CH_3)_2SiOSi(CH_3)_2(R69)$	(1,1,3,3-tetramethyl-1,3-disiloxanediy)di-3,1-propanediy] ester of [1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethoxy]acetic acid	36387-48-1
$C_{20}H_{29}F_{17}O_6Si_4$	$-OSiH(CH_3)OSiH(CH_3)OSi(R15)OSi(CH_3)_2-[(CH_2)_3OCH_2CH(OCH_2)]-$	2-[3-[2-fluoro-2-(heptafluoropropoxy)propoxy]-propyl]-2,4,6,8-tetramethyl-4-[3-oxiranymethoxy]propyl]-cyclotetrasiloxane	134251-03-9
$C_{20}H_{30}F_{12}O_4Si_4$	$[(R86)(CH_3)SiO]_4$	2,4,6,8-tetramethyl-2,4,6,8-tetrakis(3,3,3-trifluoro-2-methylpropyl)cyclotetrasiloxane	503-42-4
$C_{20}H_{30}F_{12}O_8Si_4$	$[(R83)(CH_3)SiO]_4$	2,4,6,8-tetramethyl-2,4,6,8-tetrakis[2-(2,2,2-trifluoroethoxy)ethyl]-cyclotetrasiloxane	1995-95-5
$C_{20}H_{38}F_8O_7Si_4$	$(R84)(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2(R84)$	bis(2,2,3,3-tetrafluoropropyl) ester of 3,3'-(1,1,3,3,5,5,7,7-octamethyl-1,7-tetrasiloxanediy)bispropanoic acid	674-19-1

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{21}H_{13}Cl_2F_9OSi_2$	$(R74)_3SiOSiHCl_2$	3,3-dichloro-1,1,1-tris( $\alpha,\alpha,\alpha$ -trifluoro- <i>m</i> -tolyl)disiloxane	17658-72-9
$C_{22}H_{23}F_{17}O_2Si_2$	$(R21)(CH_3)_2SiOSi(CH_3)_2(C_6H_4CH=CH_2)$	1-(4-ethenylphenyl)-3-[3,3,4,4,5,5,6,6,7,7,8,8,9,10,10,10-heptadecafluorodecyl]oxy]-1,1,3,3-tetramethyldisiloxane	159835-46-8
$C_{22}H_{32}F_6O_9Si_2$	$(R49)(CH_3)_2SiOSi(CH_3)_2(R49)$	bis(2,2,2-trifluoroethyl) ester of (1,1,3,3-tetramethyl-1,3-disiloxanediyl)di-3,1-propanediyl- <i>(trans)</i> -2-butenedioic acid	109998-09-6
$C_{22}H_{33}F_{17}OSi_2$	$(R33)(CH_3)_2SiOSi(CH_3)_2(CH_2)_7CH_3$	1-(3,3,4,4,5,5,6,6,7,7,8,8,9,10,10,10-heptadecafluorodecyl)-1,1,3,3-tetramethyl-3-octyldisiloxane	139604-00-5
$C_{22}H_{36}F_{16}O_6Si_4$	$-OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)(R42)OSi(CH_3)(R42)-$	2,2,4,4,6,8-hexamethyl-6,8-bis[3-(2,2,3,3,4,4,5,5-octafluoropentyl)propyl]-cyclootetrasiloxane	111731-11-1
$C_{22}H_{46}F_{12}O_5Si_6$	$(CH_3)_3Si[OSi(CH_3)(R5)]_4OSi(CH_3)_3$	1,1,1,3,5,7,9,11,11,11-decamethyl-3,5,7,9-tetrakis(3,3,3-trifluoropropyl)hexasiloxane	92531-92-5



TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{23}H_{26}F_{18}O_2Si_2$	$(R13)(CH_3)_2SiOSi(CH_3)_2(R45)$	[1,1,3,3-tetramethyl-1-(pentafluorophenyl)ethyl]-3-[3-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]propyl]-disiloxane	111133-53-0
$C_{24}H_{34}F_8O_9Si_2$	$(R60)(CH_3)_2SiOSi(CH_3)_2(R60)$	bis(2,2,3,3-tetrafluoropropyl) ester of (1,1,3,3-tetramethyl-1,3-disiloxanediyl)di-3,1-propanediyl-2-butenedioic acid	63263-61-6
$C_{24}H_{36}F_{10}O_5Si_6$	$(R56)(CH_3)_2Si[O(CH_3)_2Si]_4OSi(CH_3)_2(R56)$	1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-1,11-bis(pentafluorophenyl)hexasiloxane	63107-83-5
$C_{24}H_{40}F_{18}O_2Si_4$	$(CH_3)_3SiOSi(CH_3)(R5)-(R67)-Si(CH_3)(R5)OSi(CH_3)_3$	1,1'-(3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-decanediyl)bis[1,3,3,3-tetramethyl-1-(3,3,3-tripropyl)disiloxane]	41291-20-7
$C_{26}H_{22}F_4OSi_2$	$(R39)_2(CH_3)SiOSi(CH_3)(R39)_2$	1,1,3,3-tetrakis(4-fluorophenyl)-1,3-dimethyldisiloxane	128903-25-3
$C_{26}H_{42}F_{10}O_6Si_7$	$(R56)(CH_3)_2Si[O(CH_3)_2Si]_5OSi(CH_3)_2(R56)$	1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl-1,13-bis(pentafluorophenyl)heptasiloxane	63107-84-6

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{28}H_{34}F_{16}O_9Si_2$	$(R59)(CH_3)_2SiOSi(CH_3)_2(R59)$	bis(2,2,3,3,4,4,5,5-octafluoropentyl) ester of (1,1,3,3-tetramethyl-1,3-disiloxanediy)di-3,1-propanediyl 2-butenedioic acid	63263-62-7
$C_{28}H_{48}F_{16}O_8Si_4$	$[OSi(R41)(CH_3)]_4$	2,4,6,8-tetramethyl-2,4,6,8-tetrakis[3-(2,2,3,3-tetrafluoropropoxy)propyl]-cyclotetrasiloxane	111731-16-9
$C_{30}H_{18}Cl_4F_{12}OSi_2$	$(R82)_2(CH_3)SiOSi(CH_3)(R82)_2$	1,1,3,3-tetrakis(4-chloro- $\alpha,\alpha,\alpha$ -trifluoro- <i>m</i> -tolyl)-1,3-dimethyldisiloxane	2560-94-3
$C_{30}H_{24}F_4N_6OSi_2$	$(R39)_2[(N_3C_2H_2)CH_2]SiOSi[CH_2(N_3C_2H_2)](R39)_2$	1,1'-[[1,1,3,3-tetrakis(4-fluorophenyl)-1,3-disiloxanediy]bis(methylene)]bis-1H-1,2,4-triazole	101805-60-1
$C_{30}H_{36}F_{10}O_2Si_4$	$[(R13)(CH_3)_2SiOSi(CH_3)_2]_2(C_6H_4)$	1,1'-(1,4-phenylene)bis[1,1,3,3-tetramethyl-3-[2-(pentafluorophenyl)ethyl]disiloxane	120347-86-6
$C_{30}H_{38}F_{12}O_2Si_6$	$[(CH_3)_2HSi(R70)-(CH_3)_2SiOSi(CH_3)_2]_2(R70)$	1,1'-(2,3,5,6-tetrafluoro- <i>p</i> -phenylene)bis[3-[4-(dimethylsilyl)-2,3,5,6-tetrafluorophenyl]-1,1,3,3-tetramethyldisiloxane	26323-18-2

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (continued).

Empirical formula	Structural formula	Name	CAS No.
$C_{30}H_{38}F_{12}O_2Si_6$	$[(CH_3)_2HSi-(R72)-(CH_3)_2SiOSi(CH_3)_2]_2(R72)$	1,1'-(2,4,5,6-tetrafluoro- <i>m</i> -phenylene)bis[3-[3-(dimethylsilyl)-2,4,5,6-tetrafluorophenyl]-1,1,3,3-tetramethyldisiloxane	25459-27-2
$C_{30}H_{56}F_6O_5Si_2$	$(R28)(CH_3)_2SiOSi(CH_3)_2(R28)$	(1,1,3,3-tetramethyl-1,3-disiloxanediy)di-1,1,1-undecanediyl ester of trifluoroacetic acid	144885-21-2
$C_{32}H_{24}F_{14}O_3Si_2$	$(R75)(C_6H_5)_2SiOSi(C_6H_5)_2(R75)$	1,3-bis(2,2,3,3,4,4,4-heptafluorobutoxy)-1,1,3,3-tetraphenyldisiloxane	16165-56-3
$C_{34}H_{32}F_6O_7Si_2$	$(R29)(CH_3)_2SiOSi(CH_3)_2(R29)$	bis(methylenoxy-4,1-phenylene) ester of (1,1,3,3-tetramethyl-1,3-disiloxanediy)-4-(trifluoromethyl)benzoic acid	144386-06-1
$C_{34}H_{32}F_6O_7Si_2$	$(R31)(CH_3)_2SiOSi(CH_3)_2(R31)$	bis[4-(trifluoromethyl)phenyl] ester of 4,4'-[(1,1,3,3-tetramethyl-1,3-disiloxanediy)bis(methylenoxy)]-bisbenzoic acid	144386-01-6
$C_{34}H_{34}F_6N_2O_5Si_2$	$(R30)(CH_3)_2SiOSi(CH_3)_2(R30)$	4,4'-[(1,1,3,3-tetramethyl-1,3-disiloxanediy)bis(methylenoxy)]bis-[N-(trifluoromethyl)phenyl]benzamide	144386-02-7

TABLE 27. DISILOXANES CONTAINING FLUOROORGANIC AND/OR BROMOORGANIC GROUPS (concluded).

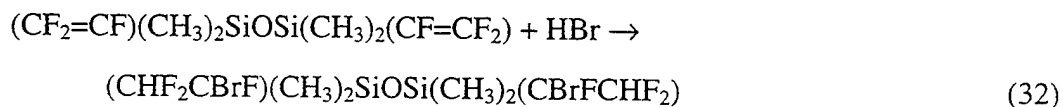
Empirical formula	Structural formula	Name	CAS No.
$C_{45}H_{36}F_6O_4Si_4$	$-(R79)(CH_3)SiO(C_6H_5)_2SiO(C_6H_5)_2SiO(C_6H_5)_2SiO-$	2-( $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexafluoro-3,5-xylyl)-2-methyl-4,4,6,6,8-hexaphenylcyclotetrasiloxane	4123-91-5
$C_{145}H_{293}F_{15}N_2O_6$	$(NH_2CH_2CH_2)(CH_3)_2Si[OSi(CH_3)(R53)]_5O-Si(CH_3)_2(CH_2CH_2NH_2)$	3,3'-[1,1,3,5,7,9,11,13,13-nonamethyl-3,5,7,9,11-pentakis(26,26,26-trifluorohexacosyl)-1,13-heptasiloxanediy]bis-1-propaneamine	96049-21-7

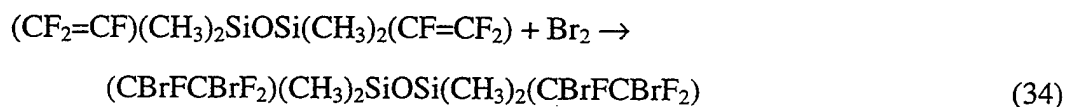
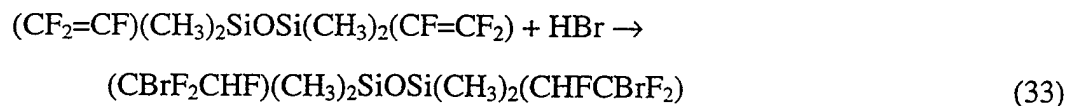
<sup>a</sup>Isomer not specified.<sup>b</sup>This structure must be polymeric.<sup>c</sup>Four different isomers reported.

## G. PROPOSED SILOXANES AND SYNTHETIC ROUTES

If available, it is proposed that the initial compounds to be tested are the three siloxanes reported with bromine-containing substituents  $\text{CH}_2=\text{CHSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{R4})$ ,  $(\text{R4}) = \text{CHBrCH}_2\text{CF}_2\text{CBrF}_2$  (CAS No. 113688-45-5);  $(\text{R7})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R7})$ ,  $(\text{R7}) = -\text{CH}_2\text{CH}_2\text{CClFCBrF}_2$  (CAS No. 5674-89-5); and  $[\text{Si}(\text{CH}_3)(\text{R11})]_4$ ,  $(\text{R11}) = -\text{CH}_2\text{CH}_2\text{CF}_2\text{BrCF}_2$  (CAS No. 32834-89-2). These specific compounds are not ideal from a molecular weight (volatility) standpoint and have a hydrogen content that is higher than desired. On the other hand, they may allow early testing of baseline materials and, contrary to expectations, could be effective fire extinguishants.

Compounds containing the unsaturated groups  $-\text{CF}=\text{CF}_2$  (R2),  $-\text{OCH}=\text{C}(\text{CF}_3)_2$  (R3),  $-\text{C}(\text{CF}_3)=\text{CF}_2$  (R20),  $-\text{CH}_2\text{CH}=\text{CF}_2$  (R63), and  $-\text{CH}=\text{CHCF}_3$  (R73) allow sites for introduction of bromine. Several siloxanes containing such groups have been reported:  $(\text{R2})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R2})$  (CAS No. 5721-28-8);  $(\text{R3})(\text{CH}_3)_2\text{SiOSiH}(\text{CH}_3)_2$  (CAS No. 17156-44-4);  $(\text{R63})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R63})$  (CAS No. 53980-28-2); and  $[(\text{R73})(\text{CH}_3)\text{SiOSi}(\text{CH}_3)_2\text{O}]_2$  (CAS No. 17913-07-4). It may be possible to introduce bromine into such groups either by addition of hydrogen bromide (HBr) or bromine ( $\text{Br}_2$ ) across the double bond. Examples are shown in Reactions 32-34 for  $(\text{R2})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R2})$ . Reactions 32 and 33 differ only on the point of attachment for the hydrogen, and reaction conditions can be used to ensure one isomer or the other. Solutions of bromine in carbon tetrachloride, chloroform, acetic acid, ether, etc., often allow facile introduction of bromine across double bonds. Hydrogen bromide is often introduced using direct addition in a suitable solvent or by photolysis. Note, however, that electron withdrawing groups, such as fluorine, will deactivate the double bond making it less reactive toward addition of HBr. On the other hand, the presence of silicon, an electron inducing substituent, may enhance the reactivity.





Condensation of compounds such as  $\text{Si}(\text{CH}_2\text{Br})(\text{CH}_3)_2\text{Cl}$  (commercially available; Reference 138) gives  $(\text{CH}_2\text{Br})(\text{CH}_3)_2\text{SiO}(\text{CH}_3)_2(\text{CH}_2\text{Br})$  (commercially available). Derivatives of the type  $\text{R}_2\text{Si}(\text{CBr}_2\text{F})\text{Cl}$ , prepared as described earlier (Reaction 24) can be coupled to give compounds of the type  $\text{R}_2(\text{CBr}_2\text{F})\text{SiOSi}(\text{CBr}_2\text{F})\text{R}_2$  (Reference 119). In addition mixed coupling of  $\text{R}_2(\text{CH}_2\text{Br})\text{SiCl}$  compounds such as  $\text{Si}(\text{CF}_3)_2(\text{CH}_3)\text{Cl}$  or  $\text{Si}(\text{CF}_3)(\text{CH}_3)_2\text{Cl}$  (Reference 117) would give  $\text{R}_2(\text{CH}_2\text{Br})\text{SiOSi}(\text{CF}_3)_2(\text{CH}_3)$  and  $\text{R}_2(\text{CH}_2\text{Br})\text{SiOSi}(\text{CF}_3)(\text{CH}_3)_2$ , though the yields could be small owing to coupling between the same groups.  $\text{Si}(\text{R}_2)$  groups (from, for example,  $\text{Si}(\text{CH}_3)(\text{CF}_3)\text{Cl}_2$ ) can also be inserted between the constituents to give trisiloxane and higher condensates such as  $\text{R}_2(\text{CBr}_2\text{F})\text{SiOSi}(\text{CH}_3)(\text{CF}_3)\text{OSi}(\text{CBr}_2\text{F})\text{R}_2$  (Reference 119).

TABLE 28. SILOXANES RECOMMENDED FOR PREPARATION AND TESTING.

Source	Compound
Compound reported	$\text{CH}_2=\text{CHSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{CHBrCH}_2\text{CF}_2\text{CBrF}_2)$
Compound reported	$(\text{CBrF}_2\text{CClFCH}_2\text{CH}_2)(\text{CH}_3)_2\text{Si}-$ $\text{OSi}(\text{CH}_3)_2(\text{CH}_2\text{CH}_2\text{CClFCBrF}_2)$
Compound reported	$[\text{Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CF}_2\text{BrCF}_2)]_4$
HBr addition to $(\text{R}2)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R}2)$	$(\text{CHF}_2\text{CBrF})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CBrFCHF}_2)$
HBr addition to $(\text{R}2)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R}2)$	$(\text{CBrF}_2\text{CHF})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CHFCBrF}_2)$
$\text{Br}_2$ addition to $(\text{R}2)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R}2)$	$(\text{CBrFCBrF}_2)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CBrFCBrF}_2)$
HBr addition to $(\text{R}3)(\text{CH}_3)_2\text{SiOSiH}(\text{CH}_3)_2$	$[\text{CH}(\text{CF}_3)_2\text{CHBrO}](\text{CH}_3)_2\text{SiOSiH}(\text{CH}_3)_2$
HBr addition to $(\text{R}3)(\text{CH}_3)_2\text{SiOSiH}(\text{CH}_3)_2$	$[\text{CBr}(\text{CF}_3)_2\text{CH}_2\text{O}](\text{CH}_3)_2\text{SiOSiH}(\text{CH}_3)_2$
$\text{Br}_2$ addition to $(\text{R}3)(\text{CH}_3)_2\text{SiOSiH}(\text{CH}_3)_2$	$[\text{CBr}(\text{CF}_3)_2\text{CHBrO}](\text{CH}_3)_2\text{SiOSiH}(\text{CH}_3)_2$
HBr addition to $(\text{R}63)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R}63)$	$(\text{CHF}_2\text{CHBrCH}_2)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2\text{CHBrCHF}_2)$
HBr addition to $(\text{R}63)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R}63)$	$(\text{CBrF}_2\text{CH}_2\text{CH}_2)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2\text{CH}_2\text{CBrF}_2)$
$\text{Br}_2$ addition to $(\text{R}63)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{R}63)$	$(\text{CBrF}_2\text{CHBrCH}_2)(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2\text{CHBrCBrF}_2)$
HBr addition to $[(\text{R}73)(\text{CH}_3)\text{SiOSi}(\text{CH}_3)_2\text{O}]_2$	$[(\text{CH}_2(\text{CF}_3)\text{CHBr})(\text{CH}_3)\text{SiOSi}(\text{CH}_3)_2\text{O}]_2$
HBr addition to $[(\text{R}73)(\text{CH}_3)\text{SiOSi}(\text{CH}_3)_2\text{O}]_2$	$[(\text{CHBr}(\text{CF}_3)\text{CH}_2)(\text{CH}_3)\text{SiOSi}(\text{CH}_3)_2\text{O}]_2$
$\text{Br}_2$ addition to $[(\text{R}73)(\text{CH}_3)\text{SiOSi}(\text{CH}_3)_2\text{O}]_2$	$[(\text{CHBr}(\text{CF}_3)\text{CHBr})(\text{CH}_3)\text{SiOSi}(\text{CH}_3)_2\text{O}]_2$

## SECTION VIII

### TOXICITY

#### A. SILANES

Silanes of major industrial importance are organochlorosilanes, methylchlorosilanes, trichlorosilane, tetrachlorosilane, phenylchlorosilanes, phenylethoxysilanes, methylethoxysilanes, and silane (Reference 139). Most of these contain direct Si-X bonds and are, therefore, strong irritants and cause pulmonary distress. In general, little is known about the toxicity of other silanes, particularly organosilanes not containing direct Si-X bonds (Reference 140). The silanes have been reported to be highly toxic by inhalation, ingestion, or skin contact, following acute exposure (Reference 139); however, this generality is likely to be due to the fact that most silanes in general use contain Si-X bonds. The American Conference of Governmental Industrial Hygienists (ACGIH) has proposed (1983/1984) a Threshold Limit Value (TLV) Time Weighted Average (TWA) exposure limits of 5 ppm ( $7 \text{ mg/m}^3$ ) for silane but no STEL value (Reference 139). Note that this is 10-fold higher than previous values set by ACGIH.

Table 29 lists toxicity information on selected silanes (References 141 and 142). Silanes with Si-X bonds and, in most cases, compounds for which no significant toxicity data (e.g., intravenous or intraperitoneal data only) were noted have been omitted. In addition, a large number of silyl amines, for which intraperitoneal  $\text{LD}_{50}$  data are available, were omitted since these compounds are not closely related to those of interest here. Cyano-, sulfonyl-, and epoxy-, and mercapto-substituted silanes were also omitted since these groups are likely to contribute to toxicity, and silicon compounds containing these groups are useful only as synthetic materials, rather than as final agents.



The SAX Hazard Rating (HR) has been given for some compounds in Table 29. This rating indicates the relative hazard for toxicity, fire, and reactivity with 3 denoting the worst hazard level. It should be noted, however, that careful consideration of the actual threat may indicate that a lower rating may be more appropriate for some compounds. For example, in some cases only toxicity by intraperitoneal, subcutaneous, and/or intravenous routes (only indirectly related to toxicities of interest here) are known. Moreover, emission of toxic combustion products, such as HBr (emitted by all or nearly all bromine-containing compounds including the present halons), appears to have been given undue weight.

TABLE 29. TOXICITY AND SAFETY INFORMATION FOR SELECTED SILANES.

Compound	Formula	CAS No.	Observations <sup>a</sup>
silane	SiH <sub>4</sub>	7803-62-5	{RTECS VV1400000} LC <sub>LO</sub> (mouse, inhalation, 4-hr) = 9600 ppm.
4-(diethoxymethylsilyl)-butylamine	Si(CH <sub>3</sub> )(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>	3037-72-7	{RTECS E04200000} LD <sub>50</sub> (rat, oral) = 6500 mg/kg. LD <sub>50</sub> (rat/mouse, skin) = 45 mg/kg, skin irritation (rabbit, 500 mg/24 hr, open) = mild. [AJA375] Poison by skin contact. Moderately toxic by ingestion. Skin irritant. EPA Extremely Hazardous Substances List. HR = 3
(4-aminobutyl)-triethoxysilane	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> -[(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> ]	3069-30-5	[AJC250] Moderately toxic by ingestion, skin contact. Skin irritant. HR = 2.
2-(triethylsiloxy)-ethylamine	Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	18419-91-5	{RTECS KR9900000} LD <sub>50</sub> (mouse, intraperitoneal) = 165 mg/kg.
2-(trimethylsiloxy)-ethylamine	Si(CH <sub>3</sub> ) <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	9804-92-2	{RTECS KS0300000} LD <sub>50</sub> (mouse, intraperitoneal) = 320 mg/kg.

TABLE 29. TOXICITY AND SAFETY INFORMATION FOR SELECTED SILANES  
(continued).

Compound	Formula	CAS No.	Observations <sup>a</sup>
(2-chloroethyl)tris(2-methoxyethoxy)silane	$\text{Si}(\text{CH}_2\text{CH}_2\text{Cl})\text{-(OCH}_2\text{CH}_2\text{OCH}_3)_3$	37894-46-5	{RTECS VV2140000} LD <sub>50</sub> (rat, oral) = 878 mg/kg.
(chloromethyl)-methyldiethoxysilane	$\text{Si}(\text{CH}_2\text{Cl})(\text{CH}_3)\text{-(OC}_2\text{H}_5)_2$	2212-10-4	{RTECS VV2180000} LC <sub>LO</sub> (rat, inhalation, 4 hr) = 2270 ppm, LD <sub>50</sub> (rat, oral) = 1300 mg/kg, skin irritation (rabbit, 500 mg/24 hr) = moderate, eye irritation (rabbit, 100 mg/24 hr) = moderate. [CIO000] Moderately toxic by ingestion, inhalation. Skin, severe eye irritant. HR = 2.
(chloromethyl)-triethoxysilane	$\text{Si}(\text{CH}_2\text{Cl})(\text{OC}_2\text{H}_5)_3$	15267-95-5	{RTECS VV2275000} LD <sub>50</sub> (rat, oral) = 2400 mg/kg, skin and eye irritation (rabbit, 500 mg/24hr) = moderate. [CIY500] Moderately toxic by ingestion. Skin, eye irritant. HR = 2.
(chloromethyl)-trimethoxysilane	$\text{Si}(\text{CH}_2\text{Cl})(\text{OCH}_3)_3$	5926-26-1	{RTECS VV2625000} LC <sub>LO</sub> (rat, inhalation, 30 min) = 3600 ppm, LD <sub>50</sub> (rat, oral) = 500 mg/kg, skin irritation (rabbit, 500 mg/24 hr) = moderate, eye irritation (rabbit, 250 µg/24 hr) = severe. [CIY750] Moderately toxic by ingestion. Mildly toxic by inhalation. Skin, severe eye irritant. HR = 2.
diethoxydimethylsilane	$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$	78-62-6	{RTECS VV3590000} LC <sub>LO</sub> (rat, inhalation, 4 hr) = 8000 ppm, LD <sub>50</sub> (rat, oral) = 9280 mg/kg, skin and eye irritation (rabbit, 500 mg/24 hr) = mild.

TABLE 29. TOXICITY AND SAFETY INFORMATION FOR SELECTED SILANES  
(continued).

Compound	Formula	CAS No.	Observations <sup>a</sup>
diethoxy[(2-ethoxy-carbonyl)ethyl]-methylsilane	$\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2\text{[CH}_2\text{CH}_2\text{C(O)OC}_2\text{H}_5\text{]}$	17963-09-6	{RTECS VV3592500} LD <sub>50</sub> (rat, oral) = 20800 mg/kg, skin irritation (rabbit, 10 mg/24 hr, open) = mild.
diethoxy[(2-ethoxy-carbonyl)propyl]-methylsilane	$\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2\text{[CH}_2\text{CH}\{\text{C(O)OC}_2\text{H}_5\}\text{CH}_3\text{]}$	6449-52-1	{RTECS VV3595000} LD <sub>50</sub> (rat, oral) = 24600 mg/kg, skin irritation (rabbit, 10 mg/24 hr) = mild.
diethoxy[(3-ethoxy-carbonyl)propyl]-methylsilane	$\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2\text{[CH}_2\text{CH}_2\text{CH}_2\text{C(O)OC}_2\text{H}_5\text{]}$	16068-01-2	{RTECS VV3597500} LD <sub>50</sub> (rat, oral) = 22400 mg/kg.
bis(2-ethylbutoxy)bis(2-ethylhexoxy)silane	$\text{Si}[\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_5]_2[\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9]_2$	10143-57-4	{RTECS VV3599000} LD <sub>50</sub> (rat, oral) = 56 g/kg.
dimethoxymethylphenyl-silane	$\text{Si}(\text{CH}_3)(\text{OCH}_3)_2(\text{C}_6\text{H}_5)$	3027-21-2	{RTECS VV3645000} LD <sub>50</sub> (rat, oral) = 892 mg/kg.
dimethylethoxyphenyl-silane	$\text{Si}(\text{CH}_3)_2(\text{OC}_2\text{H}_5)(\text{C}_6\text{H}_5)$	1825-58-7	{RTECS VV3850000} LD <sub>50</sub> (rat, oral) = 2460 mg/kg, skin and eye irritation (rabbit, 500 mg/24hr) = mild.
disilane	$\text{Si}(\text{CH}_3)_3\text{Si}(\text{CH}_3)_3$		[DXA000] Poison by inhalation. Ignites spontaneously in air. HR = 3.
[(2-ethoxycarbonyl)ethyl]-triethoxysilane	$\text{Si}(\text{OC}_2\text{H}_5)_3\text{[CH}_2\text{CH}_2\text{C(O)OC}_2\text{H}_5\text{]}$	6439-39-0	{RTECS VV4075000} LD <sub>50</sub> (rat, oral) = 22400 mg/kg, skin (rabbit, 10 mg/24hr, open) = mild.
ethoxytrimethylsilane	$\text{Si}(\text{CH}_3)_3(\text{OC}_2\text{H}_5)$	1825-62-3	{RTECS VV4110000} LC <sub>Lo</sub> (rat, inhalation, 8 hr) = 4000 ppm, LD <sub>Lo</sub> (rat, oral) = 1400 mg/kg. [EFL500] Moderately toxic by ingestion, inhalation. Eye irritant. HR = 2.

TABLE 29. TOXICITY AND SAFETY INFORMATION FOR SELECTED SILANES  
(continued).

Compound	Formula	CAS No.	Observations <sup>a</sup>
ethyltriethoxysilane	$\text{Si}(\text{C}_2\text{H}_5)(\text{OC}_2\text{H}_5)_3$	78-07-9	{RTECS VV3850000} LD <sub>50</sub> (rat, oral) = 14 g/kg, LD <sub>50</sub> (rabbit, skin) = 16 g/kg, skin irritation (rabbit, 500 mg, open) = mild.
methyltriacetoxysilane	$\text{Si}(\text{CH}_3)(\text{OC}(\text{O})\text{CH}_3)_3$	4253-34-3	{RTECS VV4500000} LD <sub>50</sub> (rat, oral) = 2060 mg/kg
methyltriethoxysilane	$\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_3$	2031-67-6	{RTECS VV4640000} LC <sub>Lo</sub> (rat, inhalation, 8 hr) = 4000 ppm, LD <sub>50</sub> (rat, oral) = 15700 mg/kg, skin and eye irritation (rabbit, 500 mg/24 hr) = mild.
methyltrimethoxysilane	$\text{Si}(\text{CH}_3)(\text{OCH}_3)_3$	1185-55-3	{RTECS VV4650000} LD <sub>50</sub> (rat, oral) = 12500 mg/kg, skin and eye irritation (rabbit, 500 mg/24 hr) = mild. [MQF500] Mildly toxic by ingestion. Skin, eye irritant.
pentyltriethoxysilane	$\text{Si}(\text{C}_5\text{H}_{11})(\text{OC}_2\text{H}_5)_3$	2761-24-2	{RTECS VV4750000} LD <sub>50</sub> (rat, oral) = 20 g/kg, LD <sub>50</sub> (rabbit, skin) = 7130 mg/kg, skin irritation (rabbit, 10 mg/24 hr, open) = mild.
pentyltrimethoxysilane	$\text{Si}(\text{C}_5\text{H}_{11})(\text{OCH}_3)_3$	2996-95-4	{RTECS VV4805000} LD <sub>50</sub> (rat, oral) = 4920 mg/kg, skin irritation (rabbit, 500 mg/24 hr, open) = mild.
phenyltriethoxysilane	$\text{Si}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_3$	780-69-8	{RTECS VV4900000} LD <sub>50</sub> (rat, oral) = 2830 mg/kg, LD <sub>50</sub> (rabbit, skin) = 3180 mg/kg.

TABLE 29. TOXICITY AND SAFETY INFORMATION FOR SELECTED SILANES  
(continued).

Compound	Formula	CAS No.	Observations <sup>a</sup>
tetraethoxysilane	$\text{Si}(\text{OC}_2\text{H}_5)_4$	78-10-4	{RTECS VV9450000} $\text{LC}_{\text{LO}}$ (guinea pig, inhalation, 6 hr) = 700 ppm, $\text{LC}_{\text{LO}}$ (rat, inhalation, 4 hr) = 1000 ppm, $\text{LD}_{50}$ (rat, oral) = 6270 mg/kg, $\text{LD}_{50}$ (rabbit, skin) = 5878 mg/kg, skin irritation (rabbit, 500 mg/24 hr) = moderate, eye irritation (rabbit, 100 mg) = mild, eye irritation (guinea pig, 2500 ppm/2 hr) = severe. [ENY600] Poisonous by intravenous. Moderately toxic by other routes. Skin, mucous membrane, severe eye irritant. Narcotic at high concentrations. Flammable.
triethoxysilane	$\text{SiH}(\text{OC}_2\text{H}_5)_3$	998-30-1	{RTECS VV9450000} $\text{LC}_{50}$ (mouse, inhalation, 2 hr) = 500 mg/m <sup>3</sup> .
triethoxyvinylsilane	$\text{Si}(\text{OC}_2\text{H}_5)_3(\text{CH}=\text{CH}_2)$	78-08-0	{RTECS VV6700000} $\text{LC}_{\text{LO}}$ (rat, inhalation, 4 hr) = 4000 ppm, $\text{LD}_{50}$ (rat, oral) = 3 g/kg, $\text{LD}_{50}$ (rabbit, skin) = 10 g/kg, skin irritation (rabbit, 500 mg, open) = mild.
trimethoxysilane	$\text{SiH}(\text{OCH}_3)_3$	2487-90-3	{RTECS VV6750000} $\text{LC}_{50}$ (rat, inhalation, 4 hr) = 125 ppm (chronic pulmonary edema), $\text{LD}_{50}$ (rat, oral) = 9330 mg/kg, $\text{LD}_{50}$ (rabbit, skin) = 6300 mg/kg.
trimethoxyvinylsilane	$\text{Si}(\text{OCH}_3)_3(\text{CH}=\text{CH}_2)$	2768-02-7	{RTECS VV6770000} $\text{LD}_{50}$ (rat, oral) = 11300 mg/kg, $\text{LD}_{50}$ (rabbit, skin) = 3540 mg/kg.

TABLE 29. TOXICITY AND SAFETY INFORMATION FOR SELECTED SILANES  
(continued).

Compound	Formula	CAS No.	Observations <sup>a</sup>
tris(2-chloroethoxy)silane	$\text{SiH}(\text{OCH}_2\text{CH}_2\text{Cl})_3$	10138-79-1	{RTECS VV6825000} $\text{LD}_{50}$ (rat, oral) = 190 mg/kg, $\text{LD}_{50}$ (rabbit, skin) = 89 mg/kg, skin irritation (rabbit, 10 mg/24 hr, open) = mild, eye irritation (rabbit, 20 mg) = severe.
tris(2-methoxyethoxy)-vinylsilane	$\text{Si}(\text{CH}_2\text{CH}_2\text{OCH}_3)_3\text{-(CH=CH}_2\text{)}$	1067-53-4	{RTECS VV6826000} $\text{LD}_{50}$ (rat, oral) = 2960 mg/kg, $\text{LD}_{50}$ (rabbit, skin) = 1500 mg/kg, skin irritation (rabbit, 500 mg, open) = mild.
diphenylmethylsilanol	$\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{OH}$	778-25-6	{RTECS VV6950000} $\text{LD}_{\text{LO}}$ (rat, oral) = 700 mg/kg.
tetrakis(2-ethylbutoxy)silane	$\text{Si}[\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{-CH}_2\text{CH}_3]_4$	78-13-7	{RTECS VV9400000} $\text{LD}_{50}$ (rat, oral) = 20 g/kg, skin irritation (rabbit, 500 mg, open) = mild.
tetrakis(2-fluoroethoxy)silane	$\text{Si}(\text{OCH}_2\text{CH}_2\text{F})_4$	650-00-0	{RTECS VV9535000} $\text{LC}_{\text{LO}}$ (guinea pig, inhalation, 10 min) = 100 $\text{mg/m}^3$ .
tetramethoxysilane	$\text{Si}(\text{OCH}_3)_4$	681-84-5	{RTECS VV9800000} $\text{LC}_{\text{LO}}$ (mouse, inhalation, 10 min) = 1000 $\text{mg/m}^3$ , $\text{LC}_{\text{LO}}$ (rat, inhalation, 4 hr) = 250 ppm, $\text{LD}_{\text{LO}}$ (rat, oral) = 700 mg/kg, $\text{LD}_{50}$ (rabbit, skin) = 17 g/kg, eye irritation (rabbit, 250 $\mu\text{g}$ ) = severe.
ethyltriethoxysilane	$\text{Si}(\text{C}_2\text{H}_5)(\text{OC}_2\text{H}_5)_3$	78-07-9	[EQA000] $\text{LD}_{50}$ (rat, oral) = 14 g/kg, $\text{LD}_{50}$ (rabbit, skin) = 16 g/kg. Mildly toxic by ingestion, skin contact. HR = 1.

TABLE 29. TOXICITY AND SAFETY INFORMATION FOR SELECTED SILANES  
(continued).

Compound	Formula	CAS No.	Observations <sup>a</sup>
phenyltriethoxysilane	$\text{Si}(\text{OC}_2\text{H}_5)_3(\text{C}_6\text{H}_5)$	780-69-8	[PGO000] LD <sub>50</sub> (rat, oral) = 2830 mg/kg, LD <sub>50</sub> (rabbit, skin) = 3180 mg/kg. Moderately toxic by ingestion, skin contact. HR = 2.
trimethoxysilane	$\text{SiH}(\text{OCH}_3)_3$	2487-90-3	[TLB750] LC <sub>50</sub> (rat, inhalation, 4 hr) = 125 ppm, LD <sub>50</sub> (rat, oral) = 9330 mg/kg, LD <sub>50</sub> (rabbit, skin) = 6300 mg/kg. Moderately toxic by inhalation. Mildly toxic by ingestion, skin contact. HR = 2.
trimethoxyvinylsilane	$\text{Si}(\text{OCH}_3)_3(\text{CH}=\text{CH}_2)$	2768-02-7	[TLD000] LD <sub>50</sub> (rat, oral) = 11,300 mg/kg, LD <sub>50</sub> (rabbit, skin) = 3540 mg/kg. Moderately toxic by skin contact. Mildly toxic by ingestion. HR = 2.
tris(2-chloroethoxy)silane	$\text{SiH}(\text{OCH}_2\text{CH}_2\text{Cl})_3$	10138-79-1	[TNF000] LD <sub>50</sub> (rat, oral) = 190 mg/kg, LD <sub>50</sub> (rabbit, skin) = 89 mg/kg. Poison by ingestion, skin contact. Skin, severe eye irritant. HR = 3.

<sup>a</sup>The SAX Number (Reference 141) is given in brackets followed by information from that reference; the RTECS Number (Reference 142) is given in braces, again followed by information from that source. "Open" denotes the test patch used in skin irritation studies is not occluded (isolated from the atmosphere). "HR" = SAX Hazard Rating.

## B. SILOXANES

Relatively little toxicological and related information is available on pure siloxanes (Table 30; Reference 141), although a large amount is available for siloxane polymeric oils under tradenames. Note that very large differences in the hazard ratings are reported for

hexamethyldisiloxane listed under two different names. For the most part, the polymeric siloxanes, in particular, the methylpolysiloxanes have rather low toxicities. In most cases, the LD<sub>50</sub> for oral routes are greater than 10 g/kg of body weight. Where significant toxicity or irritation is observed, it is often due to the presence of reactive termination groups on the polysiloxane chain. Some methylpolysiloxanes have been reported to be tumorigens (Reference 141).

TABLE 30. DANGEROUS PROPERTIES OF SILOXANES.

Compound	Formula	CAS No.	Observations <sup>a</sup>
hexamethyldisiloxane (designated bistrimethylsilyl oxide)	(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>3</sub>		[BLR250] Dangerous fire hazard. Flash point = -1 °C. HR = 3.
hexamethyldisiloxane	(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>3</sub>	107-46-0	[HEE000] LD <sub>LO</sub> (guinea pig, oral) = 50 g/kg. Mildly toxic by ingestion and intraperitoneal. Skin irritant. HR = 1.

<sup>a</sup>The SAX Number (Reference 141) is given in brackets. "HR" = SAX Hazard Rating.

### C. COMBUSTION BYPRODUCTS

Silicosis, a pulmonary fibrosis, is possible on long-term exposure to silica, SiO<sub>2</sub> (Reference 140), one of the products expected from interaction of silicon compounds with fires; however, this results primarily from chronic exposure and is, therefore, unlikely to be a significant toxicological barrier to the use of silicon compounds as fire extinguishants.



SECTION IX  
SILICON/NITROGEN COMPOUNDS

There has been a large increase in studies of compounds containing nitrogen-silicon bonds. Many of these compounds are highly stable, and there is a possibility that derivatives of such compounds could provide candidates for halon alternatives. Much of the earlier work was on linear structures; however, the cyclic silazanes (Figure 13) have been of significant interest (References 143 and 144). Much of the recent work has emphasized the four-membered ring compounds (Reference 145). Structurally, the compounds resemble the siloxanes, with the oxygen atom being replaced by the isoelectronic NH group.

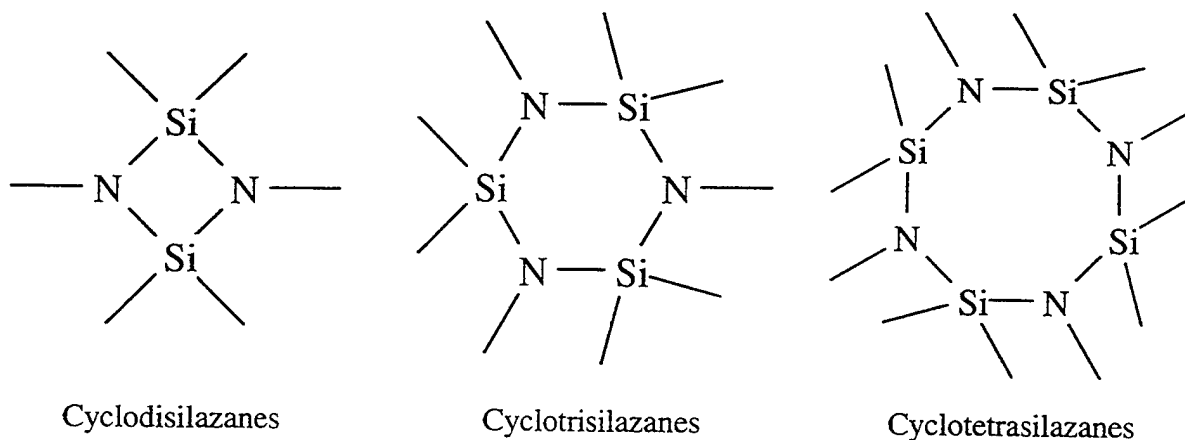


Figure 13. Cyclosilazanes.

## SECTION X

### TESTING

#### A. MATERIALS

The compounds shown in Table 31 are commercially available (Reference 138).

TABLE 31. COMMERCIALY AVAILABLE BROMOCARBON -SUBSTITUTED SILICON COMPOUNDS.

Compound	Structure	Properties	<sup>a</sup> Price
bromomethyltrimethylsilane	$\text{Si}(\text{CH}_2\text{Br})(\text{CH}_3)_3$	BP = 116-117 °C, flammable	£96/25g
(3-bromopropyl)-trichlorosilane	$\text{Si}(\text{CH}_2\text{BrCH}_2\text{CH}_2)\text{Cl}_3$	BP = 85 °C (16 Torr), combustible, moisture sensitive	£16.70/10g £70.80/50 g
(bromomethyl)dimethylchlorosilane	$\text{Si}(\text{CH}_2\text{Br})(\text{CH}_3)_2\text{Cl}$	BP = 130 °C (730 Torr), corrosive	£12/10g £30/50g
(bromomethyl)trimethylsilane	$\text{Si}(\text{CH}_2\text{Br})(\text{CH}_3)_3$	BP = 145-148 °C (10 Torr), flammable	£110.29/10g £217.45/25g
trimethylsilyl bromoacetate	$\text{CH}_2\text{BrCOOSi}(\text{CH}_3)_3$	BP = 57-58 °C, flammable, corrosive	£12/25g £44.40/100g
(1-bromovinyl)-trimethylsilane	$\text{Si}(\text{CBr}=\text{CH}_2)(\text{CH}_3)_3$	BP = 55 °C (80 Torr)	£91.26/5g £315.45/25g
(2-bromovinyl)-trimethylsilane	$\text{Si}(\text{CH}=\text{CHBr})(\text{CH}_3)_3$	BP = 50-51 °C (52 Torr), flammable	£99.47/5g £397.88/25g
vinyl(bromomethyl)dimethylsilane	$\text{Si}(\text{CH}_2\text{Br})(\text{CH}=\text{CH}_2)(\text{CH}_3)_2$	BP = 40-42 °C (20 Torr), hydrolytic sensitivity	£85.26/5g £341.04/25g
bromophenyltrichlorosilane	$\text{Si}(\text{C}_6\text{H}_4\text{Br})\text{Cl}_3$	BP = 106-108 °C (6 Torr), corrosive, moisture sensitive	£30.99/25g £90/100g
3-bromo-1-(trimethylsilyl)-1-propyne (95%)	$\text{Si}(\text{C}\equiv\text{CCH}_2\text{Br})(\text{CH}_3)_3$	BP = 44-45 °C (2 Torr), hydrolytic sensitivity	£34.50/1g £138/5g

TABLE 31. COMMERCIALY AVAILABLE BROMOCARBON -SUBSTITUTED SILICON COMPOUNDS (concluded).

Compound	Structure	Properties	<sup>a</sup> Price
(3-bromopropyl)-trimethoxysilane	$\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Br})(\text{OCH}_3)_3$	BP = 130 °C (45 Torr), combustible, moisture sensitive	£60/10g £232/50g
1,3-bis(bromomethyl)-tetramethyldisiloxane	$[(\text{CH}_2\text{Br})(\text{CH}_3)_2\text{Si}]_2\text{O}$	BP = 102-104 °C (15 Torr), combustible	£56.40/25g £160/100g
(8-bromooctyl)-trichlorosilane	$\text{Si}[\text{CH}_2(\text{CH}_2)_6\text{CH}_2\text{Br}]\text{Cl}_3$	BP = 145-148 °C (10 Torr), flammable	£110.29/10g £217.45/25g
(4-bromophenoxy)-trimethylsilane	$\text{Si}(\text{OC}_6\text{H}_4\text{Br})(\text{CH}_3)_3$	BP = 126 °C (25 Torr), flammable	£25/25g
(bromophenyl)trimethoxysilane (mixed isomers)	$\text{Si}(\text{C}_6\text{H}_4\text{Br})(\text{OCH}_3)_3$	BP = 136 °C (13.5 Torr), combustible, irritant	£25/10g £95/50g
(8-bromooctyl)-trimethoxysilane	$\text{Si}[\text{CH}_2(\text{CH}_2)_6\text{CH}_2\text{Br}](\text{OCH}_3)_3$	BP = 100-101 °C (0.2 Torr), flammable	£119.46/10g £238.87/25g
(bromophenyl)triethoxysilane (mixed isomers)	$\text{Si}(\text{C}_6\text{H}_4\text{Br})(\text{OCH}_2\text{CH}_3)_3$	combustible, irritant	£25/10g £95/50g

<sup>a</sup>All prices are in £ Sterling, UK.

(Trifluoromethyl)trimethylsilane,  $\text{Si}(\text{CF}_3)(\text{CH}_3)_2$ , was synthesized by the method of Pawelke (Reference 118). Chlorotrimethylsilane,  $\text{Si}(\text{CH}_3)_3\text{Cl}$  (48.5 g, 0.45 mol), was dissolved in 500 mL benzonitrile in a 3-neck round bottom flask. The flask was cooled in liquid nitrogen, and trifluoriodomethane  $\text{CF}_3\text{I}$  (157.9 g, 0.81 mol) was condensed onto the benzonitrile over a period of two hours. The flask was wrapped in ceramic blanket insulation and allowed to warm

up slowly. When the solution reached  $-18\text{ }^{\circ}\text{C}$ , tetrakis(dimethylamino)ethylene,  $(\text{CH}_3)_2\text{NC}=\text{CN}(\text{CH}_3)_2$  (100 g, 0.50 mol) was added dropwise over a period of about 40 minutes. The reaction mixture was then allowed to stir overnight at room temperature.

The reaction mixture was filtered to remove the insoluble salt of  $(\text{CH}_3)_2\text{NC}=\text{CN}(\text{CH}_3)_2$ , and the volatile products removed by distillation in vacuo. The fraction distilling at  $40$  to  $53\text{ }^{\circ}\text{C}$  at 120 Torr was collected. The final yield of 29.8 g corresponding to 47 percent of theoretical for  $(\text{CH}_3)_3\text{SiCF}_3$ , was low due to mechanical losses during the distillation. The product was noted to fume strongly in air. Analysis by GC/MS was performed; however, the results were inconclusive, possibly due to instrument failure.

## TESTING

Some commercially available silicon-containing compounds were tested at laboratory scale to determine their effectiveness in extinguishing hydrocarbon flames. The recognized laboratory-scale fire suppression test method uses the cup-burner apparatus. The original cup burner, developed by Hirst and Booth (Reference 146) at Imperial Chemical, Inc. (ICI), in the late 1970s, required relatively large test quantities of chemicals. In an effort to reduce the amount of chemicals needed to test the flame suppression capabilities, NMERI has developed and validated a 5/8-scale version of the ICI apparatus under a separate effort. The equipment and test technique are fully described elsewhere (Reference 147).

Cup-burner tests were carried out on several commercially available compounds using the NMERI 5/8-scale cup burner—chlorotrimethylsilane ( $\text{SiCl}(\text{CH}_3)_3$ ), dichlorodimethylsilane ( $\text{SiCl}_2(\text{CH}_3)_2$ ), octamethylcyclotetrasiloxane ( $(\text{OSi}(\text{CH}_3)_2)_4$ ), tetraethoxysilane ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), hexaethyldisiloxane ( $(\text{C}_2\text{H}_5)_3\text{SiOSi}(\text{C}_2\text{H}_5)_3$ ), and 1,3-bis(bromomethyl)tetramethyldisiloxane ( $(\text{CH}_2\text{Br})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2\text{Br})$ ). None of these (with the possible exception of the last compound) was expected to be a candidate for halon replacement; however, testing was needed to gain experience in the handling and testing of silicon compounds.

All compounds were tested with mixing chamber temperatures of  $20$ - $40\text{ }^{\circ}\text{C}$  above their boiling points. Of the six compounds listed, the first five ignited in the cup burner leaving a

white deposit, presumed to be  $\text{SiO}_2$ , in the apparatus. Although no quantifiable results were obtained, the last compound, 1,3-bis(bromomethyl)tetramethyldisiloxane, showed some promise. The boiling point for this compound is listed as 102 to 104 °C at 15 Torr, but at a chamber temperature of >240 °C the compound was still not completely volatilized. This material does not appear to be combustible and will be tested using the laboratory-scale discharge extinguishment (LSDE) apparatus (Reference 148).

Three other compounds were not tested in the cup burner. Tetramethoxysilane was obviously flammable in preliminary testing (a pool could be ignited with a match), and hexamethylcyclotrisiloxane is a solid. A cotton swab dipped into (trifluoromethyl)-tri-methylsilane ( $\text{Si}(\text{CF}_3)(\text{CH}_3)_2$ ) ignited easily and burned with a generation of dense white smoke.

## SECTION XI

### RESULTS AND CONCLUSIONS FROM THE TECHNOLOGY REVIEW

This study has concentrated on silanes and siloxanes as being the most likely candidates for silicon-based fire retardants. It is found that higher order silanes, i.e., those containing more than about five Si-Si units in the silane chain, are basically unstable and revert spontaneously (at temperatures near and above room temperature) to lower order silanes, with highly combustible monosilane ( $\text{SiH}_4$ ) being the dominant product. Due to the reactivity of Si-H bonds with oxygen, silicon compounds possessing such bonds do not appear to be good candidates for fire suppressants. The Si- $\text{CH}_3$  bond reacts similar to the Si-H bond, although not as vigorously, and, in particular, this bond appears to be quite stable in the methyl siloxanes.

Substitution of halogen atoms (fluorine, chlorine, bromine, or iodine) for the hydrogen atoms in silanes creates more stable compounds; however, these halosilanes readily hydrolyze to produce toxic hydrogen halides ( $\text{HF}$ ,  $\text{HBr}$ ,  $\text{HCl}$ , and  $\text{HI}$ ). Substitution of methyl radicals for hydrogen and/or the halogens bonded directly to the silicon and, more attractively, by (halogenated-methyl) radicals potentially provides a series of compounds having lowered toxicity, decreased flammability, and decreased corrosiveness as compared to the silanes and the halogenated silanes.

The siloxanes can be synthesized to give stable chains containing  $(\text{CH}_3)_2\text{SiO}$  units that are relatively inert for very large chains (1000 units or more), but which also exhibit increasing viscosity as the chain lengthens. These are silicone oils, and as such have many of the properties of a classical oil, such as flash points, thermal degradation, etc., although the methypolysilicones are thermally quite stable for temperatures up to 200 °C. The chains having low numbers of basic units with quite low viscosity also have low flash points and thus would tend to provide fuel to an open flame (though, of course, this could presumably be overcome by substitution with fluorine and/or bromine). The chemical nature of siloxanes tends to be insensitive to the chain length and structure and to depend more on the precise chemical nature of the radicals attached to the Si atoms. By modifying the methyl groups (by introducing halogen atoms), it is possible to

produce a system that could provide bromine for fire suppression. The concern for this species is the high boiling point of the siloxanes and their emission of combustible vapors when heated moderately in the presence of oxygen.

A thorough review of the literature on silicon compounds has been made. Two families of compounds—silanes and siloxanes—have been emphasized. The substances of greatest interest are those in which the R group contains a bromine or iodine atom. No compounds containing halogen atoms connected directly to silicon have been considered as candidates; however, such compounds may be examined as baseline materials. In general, the greater the amount of hydrogen (as opposed to halogens) in the molecules, the greater will be the volatility. But this also can lead to increased flammability and decreased effectiveness as a fire extinguishing agent. From a toxicological standpoint, fluorine is better than chlorine. Thus, the molecules containing a bromine atom on an alkyl substituent and fully or partially fluorinated substituents (either alkyls or alkoxides) are targeted. It may be possible to allow compounds containing hydrogen atoms directly bonded to silicon.

Silanes, particularly those containing Si-H bonds, are less suitable than siloxanes as a basis for fire suppressants. The Si-H bond is vulnerable to oxidation upon heating and exposure to air or water. Thus, Si-H bonds would be replaced by Si-C or Si-O bonds. Even the methylsilanes tend to be reactive. Most of them are flammable and/or corrosive, both characteristics being undesirable for fire extinguishants.

In some ways, silanes look less promising than siloxanes as parent compounds for preparation of bromine-containing fire extinguishants. Siloxanes tend to be less reactive, have lower toxicities, and are easier to prepare. However, siloxanes have one major drawback. Their molecular weights tend to be higher and, therefore, their volatilities and viscosities may be less favorable. Some silanes have been identified that show significant promise as parent materials.

Table 32 presents those silicon compounds most likely to have the properties needed for a halon replacement. This list is subject to change depending on results of further study. Note that these are optimal from preliminary considerations of structural features. Availability may be an equally important determining factor.



TABLE 32. MOST PROMISING SILICON CANDIDATES.

Silanes	Siloxanes
$\text{Si}(\text{CF}_3)_3(\text{CF}_2\text{Br})$	$(\text{CH}_2\text{Br})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2\text{Br})$
$\text{Si}(\text{CF}_3)_3(\text{CHFBr})$	$(\text{CH}_2\text{Br})_2(\text{CH}_3)\text{SiOSi}(\text{CH}_3)(\text{CH}_2\text{Br})_2$
$\text{Si}(\text{CH}_2\text{CF}_3)_3(\text{CF}_2\text{Br})$	$(\text{CF}_2\text{Br})(\text{CF}_3\text{CH}_2)_2\text{SiOSi}(\text{CH}_2\text{CF}_3)_2(\text{CF}_2\text{Br})$
$\text{Si}(\text{CH}_2\text{CF}_3)_3(\text{CHFBr})$	$(\text{CF}_2\text{Br})(\text{CF}_3)_2\text{SiOSi}(\text{CF}_3)_2(\text{CF}_2\text{Br})$
$\text{Si}(\text{OCH}_2\text{CF}_3)_3(\text{CF}_2\text{Br})$	$(\text{CH}_2\text{Br})_3\text{SiOSi}(\text{CH}_2\text{Br})_3$

One final result that came out of this study is that the boiling points for a large number of silicon compounds are remarkably similar to those found for the carbon analogs (Table 33). This implies that in many cases, one can estimate the boiling point (an exceedingly important property) from that of the corresponding carbon compound, the latter being more likely to be known.

TABLE 33. COMPARISON OF THE BOILING POINTS OF SILICON AND CARBON COMPOUNDS OF SIMILAR STRUCTURE.

Type formula	Boiling point, °C	
	T = Si	T = C
$(\text{CH}_3)_3\text{TCl}$	58	52
$(\text{CH}_3)_3\text{T-OH}$	99	83
$(\text{CH}_3)_3\text{T-OCH}_3$	57	55
$(\text{CH}_3)_3\text{T-OC}_2\text{H}_5$	75	73
$(\text{CH}_3)_3\text{T-OC}_4\text{H}_9\text{-n}$	124	124
$(\text{CH}_3)_3\text{T-O-T}(\text{CH}_3)_3$	100	107
$(\text{CH}_3)_3\text{T-NH-T}(\text{CH}_3)_3$	126	92-95

## SECTION XII

### RECOMMENDATIONS

1. The compounds shown in Table 32 were prepared or obtained and their fire extinguishment properties measured using cup burner and premixed flat-flame burner experiments. The premixed flat-flame burners allow heat extraction and extinguishment measurements under a variety of conditions (atmospheric and low pressure, heated and ambient temperature). The advantage of the premixed flat-flame burner burners (e.g., the Sapphire apparatuses [Reference 149]) is that they can quantify extinguishment rate and allow calculations of the degree of physical and chemical contributions. The results should be used to define relationships between extinguishment performance and structure.

2. Photochemical cross sections should be determined. A major question is whether silicon compounds containing bromocarbon groups have an enhanced photochemical cross section relative to similar non-silicon-containing bromocarbons. In the preliminary estimations of lifetimes in this project, this was not taken into account. Additional review and, possibly, some laboratory studies are needed to answer this question. Cross sections for absorption of UV radiation (largely at wavelengths above 280 nm) and quantum yields for photolytic dissociation should be determined for one or more bromocarbon-substituted silanes and siloxanes as functions of both wavelength and temperature.

3. The experimental toxicity of selected compounds, with an emphasis on those in Table 32, should be determined. Little or no toxicity information is available for any of these compounds. Toxicity testing should be relatively low cost since cardiac sensitization testing is almost certainly not needed. The cost for  $LC_{50}$  or  $LC_{LO}$  testing is expected to be approximately \$15,000 per compound.

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## APPENDIX A

### GLOSSARY

**Aliphatic**—Straight-chain, branched-chain, or cyclic structures containing carbon atoms linked by single  $sp^3$ - $sp^3$  bonds.

**Alkoxy**—A group of the type -OR, where R is an aliphatic hydrocarbon radical or a substituted aliphatic radical. Examples are methoxy (-OCH<sub>3</sub>) and ethoxy (-OC<sub>2</sub>H<sub>5</sub>).

**Alkoxysilane**—An alkoxy derivative of a silane giving a compound having at least one Si-OR linkage, where R is an alkyl.

**Alkyl**—An aliphatic substituent. Examples are methyl (-CH<sub>3</sub>), ethyl (-CH<sub>2</sub>CH<sub>3</sub> or -C<sub>2</sub>H<sub>5</sub>), *n*-propyl (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> or -C<sub>3</sub>H<sub>7</sub>), *i*-propyl (-CH(CH<sub>3</sub>)<sub>2</sub>), *n*-butyl (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> or -C<sub>4</sub>H<sub>9</sub>), *t*-butyl (-C(CH<sub>3</sub>)<sub>3</sub>).

**Allyl**—The -CH<sub>2</sub>-CH=CH<sub>2</sub> group.

**Aromatic**—Cyclic molecules or fused cyclic molecules containing formally alternating single and double bonds with delocalized  $\pi$  electrons. The most common simple aromatic compound is benzene.

**Aryloxy**—A group of the type -OR, where R is an aryl group. Examples are phenoxy (-OC<sub>6</sub>H<sub>5</sub>) and naphthoxy (-OC<sub>10</sub>H<sub>7</sub>).

**Aryl**—Aromatic substituents derived from benzene and related compounds. Examples are phenyl (-C<sub>6</sub>H<sub>5</sub>), tolyl (-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), and naphthyl (-C<sub>10</sub>H<sub>7</sub>).

**Benzyl**—The phenyl-substituted methyl group, -CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, a predominantly aliphatic radical.

**Bromosilane**—A bromine derivative of a silane; a compound of silicon containing at least one Si-Br bond.

**Chlorosilane**—A chlorine derivative of a silane; a compound containing at least one Si-Cl bond.



**Covalent**—Bonding in which electrons are shared by two atoms, both of which contribute to the bonding pair(s).

**Cross-Linked**—Having a polymeric structure consisting of chains joined together by bridges or cross links that limit polymer flexibility.

**Cyclic**—Arranged in a closed ring rather than an open chain.

**Difunctional**—In a polymer-producing reaction, the term applied to a reactant possessing two functional groups and, therefore, capable of propagating a chain to form a linear polymer.

**Disilane**—The compound  $\text{Si}_2\text{H}_6$  or derivatives thereof.

**Disproportionation**—Chemical reactions in which some molecules of a single compound are increased in size (or oxidation state) and other molecules are reduced in size (or oxidation state); a reaction of the type  $2\text{A} \rightarrow \text{B} + \text{C}$ , where B and C differ in size or oxidation.

**Dissociation**—The separation of a molecule into atomic or ionic fragments when exposed to heat, electric energy, or a solvent.

**Endothermic**—A term applied to any process during which heat is absorbed.

**Exothermic**—A term applied to any process during which heat is released.

**Ester**—A compound formed from an alcohol and an oxyacid by elimination of water. Here this term is used specifically to describe an alkoxysilane or aryloxysilane, which could be considered to result from the combination of an alcohol with the hypothetical silicic acids. A compound comprising the structure  $\text{SiOR}$  where R is an organic group.

**Ethyl**—The  $-\text{C}_2\text{H}_5$  group, second of the homologous series of saturated aliphatic radicals of the type  $\text{C}_n\text{H}_{2n+1}$ .

**Fluorosilane**—A fluorine derivative of a silane. A compound of silicon (other than fluorosilicic acid or a fluorosilicate) containing at least one Si-F linkage.

**Halide**—A compound a halogen atom. Alternatively, a negative ion of one of the halogen atoms (e.g., fluoride,  $F^-$ ; chloride,  $Cl^-$ ; bromide,  $Br^-$ ; or iodide,  $I^-$ ).

**Haloalkane**—Saturated halocarbons containing only carbon, halogen, and, in some cases, hydrogen atoms.

**Haloalkoxy**—A group of the type  $-OR$ , where R is an aliphatic hydrocarbon group or a substituted aliphatic group containing one or more halogen atoms. Examples are chloromethoxy ( $-OCH_2Cl$ ) and 2-bromoethoxy ( $-CH_2CH_2Br$ ).

**Haloalkyl**—An aliphatic substituent containing one or more halogen atoms. Examples are tribromomethyl ( $-CBr_3$ ) and 2-chloroethyl ( $-CH_2CH_2Cl$ ).

**Halocarbon**—A compound of carbon and one or more halogen atoms with or without hydrogen.

**Halogen**—One of the elements or atoms fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The last element is radioactive and is not considered in this project.

**Halosilane**—A halogen derivative of a silane. A compound of silicon containing at least one Si-X bond, where X is a halogen atom.

**Homolog**—A compound forming part of a homologous series, and hence closely related to the other compounds in that series in structure, composition, and physical properties.

**Homologous**—An adjective used for homologs.

**Hydride**—A binary compound of hydrogen with some other element.

**Hydrocarbon**—A binary compound of carbon and hydrogen. This term includes aliphatic compounds (paraffins), compounds containing double bonds (olefins), and aromatics.

**Hydrochlorofluorocarbon**—An aliphatic compound containing only hydrogen, fluorine, chlorine, and carbon. An example is HCFC-123,  $CHCl_2CF_3$ .

**Hydrofluorocarbon**—An aliphatic compound containing only hydrogen, fluorine, and carbon. An example is HFC-134a,  $\text{CH}_2\text{FCF}_3$ .

**Hydrolysis**—The reaction of a material with water. Here, the most general example is the reaction of a silicon halide with water, e.g.,  $\text{SiR}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{SiR}_3\text{OH} + \text{HCl}$ .

**Hydroxyl**—The  $-\text{OH}$  group, common to alcohols,  $\text{ROH}$ , and water or the unattached  $\bullet\text{OH}$  free radical.

**Iso**—Here, an adjective designating a 3-carbon alkyl group attached at the middle carbon atom. The isopropyl group (also designated as the *i*-propyl group) is  $-\text{CH}(\text{CH}_3)_2$ .

**Linear Polymer**—A polymer derived from monofunctional and bifunctional units and, therefore, consisting of straight-chain or coiled-linear molecules rather than a cross-linked or three-dimensional network.

**Methyl**—The  $-\text{CH}_3$  group, simplest member of the homologous series of saturated aliphatic radicals of the type  $\text{C}_n\text{H}_{2n+1}$ .

**Normal**—An adjective designating a group comprised of a straight chain. For example, the normal-butyl group (usually designated as an *n*-butyl group) is  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ .

**Olefin**—An unsaturated hydrocarbon containing one or more double bonds. An example is ethene (ethylene),  $\text{H}_2\text{C}=\text{CH}_2$ .

**Organosilicon**—A compound of silicon containing one or more organic substituents. Often the term “organosilicon” is reserved for compounds containing one or more C-Si bonds (as distinguished from esters, which contain an oxygen atom between the carbon and silicon atoms, e.g., C-O-Si).

**Organosiloxane**—A siloxane containing one or more organic substituents. Often this term is reserved for siloxanes containing one or more C-Si bonds.

**Oxidation**—The removal of electrons from an atom or ion making its charge more positive or less negative. In a more restricted sense, chemical combination with oxygen. Oxidation is also used as an adjective to describe the formal contribution of electrons to a bond as in oxidation state or oxidation number.

**Perfluorocarbon**—An aliphatic compound containing only fluorine and carbon. An example is FC-218 (sometimes called PFC-218),  $\text{CF}_3\text{CF}_2\text{CF}_3$ .

**Phenyl**—The cyclic  $-\text{C}_6\text{H}_5$  group derived from benzene.

**Phosphorus Nitride**—A compound containing phosphorus and nitrogen including such families as phosphazenes, phosphonitriles, and phosphazanes.

**Pi ( $\pi$ ) Bonding**—Bonding involving “sideways” overlap of atomic orbitals as opposed to sigma ( $\sigma$ ) bonding.

**Polymer**—A chemical compound in which some relatively simple unit structure or group is repeated throughout the molecules.

**Propargyl**—The  $\text{HC}\equiv\text{CCH}_2-$  group

**Propyl**—The  $-\text{C}_3\text{H}_7$  group, third in the homologous series of saturated aliphatic radicals of the type  $\text{C}_n\text{H}_{2n+1}$ .

**Pyrolysis**—One type of thermal dissociation in which molecules split into simpler fragments upon heating.

**Resin**—A (usually) organic material that is characterized by being amorphous, isotropic, or plastic.

**Saturated**—Chemically combined to the extent allowed by the most commonly exhibited valence. Containing no double or triple bonds.

**Sigma ( $\sigma$ ) Bonding**—Bonding involving direct, end-on overlap of atomic orbitals.

**Silane**—Hydrides of silicon of the type  $\text{Si}_n\text{H}_{2n+2}$  or derivatives thereof.

**Silanol**—Silicon compounds containing a Si-OH bond. Here we include diols (compounds containing two such bonds) and triols (three such bonds) under the general heading of silanols.

**Silicate**—Inorganic silicates are minerals containing silicon, oxygen, one or more metals, and, sometimes, hydrogen. Occasionally, some organic compounds are referred to as silicates to denote their relationship to the hypothetical compound,  $\text{Si}(\text{OH})_4$ .

**Silicic Acid**—Hydrated silica gel,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , sometimes (misleadingly) written as the hypothetical acid  $\text{Si}(\text{OH})_4$ .

**Silicol**—A hydroxyl derivative of silane (e.g., a silanol). A compound containing at least one Si-OH bond.

**Silicone**—A polymeric organosiloxane composed of the units  $-\text{SiR}_2-\text{O}-\text{SiR}_2-$ , where R is a hydrocarbon group or a derivative of a hydrocarbon group. This is the same as a siloxane.

**Siloxane**—A compound of silicon containing alternating silicon and oxygen atoms. Examples are disiloxane,  $\text{H}_3\text{Si}-\text{O}-\text{SiH}_3$ , trisiloxane,  $\text{H}_3\text{Si}-\text{O}-\text{SiH}_2-\text{O}-\text{SiH}_3$ , etc. This is the same as a silicone.

**Silyl**—The  $-\text{SiH}_3$  group or a derivative of this group. An example is trimethylsilyl,  $-\text{Si}(\text{CH}_3)_3$ .

**Tetramer**—A molecule consisting of four identical joined units. An example is octamethylcyclotetrasiloxane,  $[(\text{CH}_3)_2\text{SiO}]_4$ , the cyclic tetramer of methyl silicone.

**Tertiary**—An adjective designating a 4-carbon alkyl group containing one carbon attached to three others. The tertiary butyl group (also designated as the *t*-butyl or *tert*-butyl group) is  $-\text{C}(\text{CH}_3)_3$ .

**Transition State**—The intermediate state or the intermediate short-lived species that exists momentarily when reactants form products in a chemical reaction.

**Trifluoromethyl**—The  $\text{-CF}_3$  group, derived from the methyl group,  $\text{-CH}_3$ , by substitution with fluorine.

**Trimethylsilyl**—The  $\text{-Si(CH}_3)_3$  group, derived from the silyl group,  $\text{-SiH}_3$ , by substitution with methyl groups.

**Tropodegradable**—An adjective applied to compounds that are rapidly removed from the earth's troposphere by such mechanisms as photolysis, reaction with hydroxyl free radical, rainout, and physical removal.

**Unsaturated**—Containing one or more double or triple bonds. Also used to denote that further bonding is possible for one or more of the elements present in a compound.

**Valence**—A whole number that gives the combining power of an element with other elements. For covalent compounds, the valence is the number of bonds, with a double bond counting as two and a triple bond counting as three, that an atom can form with other atoms. For example, in  $\text{CH}_4$  and  $\text{O}=\text{C}=\text{O}$ , carbon has a valence of four (it is said to be tetravalent). This is the only valence observed for carbon except in some very rare solid state metal compounds and unstable, short-lived gaseous species. Silicon is usually tetravalent; however, it is also occasionally hexavalent (e.g.,  $\text{SiF}_6^{2-}$ ), and short-lived pentavalent transition state species are believed to exist.

**Vinyl**—The  $\text{-CH=CH}_2$  group.